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PART VI

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CROSSLINKING SYSTEMS FOR AROMATIC HETEROCYCLIC POLYMERS

THE UNIVERSITY OF IOWA
IOWA CITY, IOWA 52242

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This technical report has been reviewed and is approved.

Frederick L. Hedberg
Project Monitor

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Chief, Polymer Branch
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The research described in this report is directed toward the development of a universal crosslinking agent for aromatic and aromatic heterocyclic polymers. The syntheses of materials capable of forming reactive intermediates at elevated temperature are discussed. Initial experiments on the crosslinking capabilities of several crosslinking agents are discussed.

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20.

Investigation into the use of peroxides as crosslinking additives involves the synthesis of high molecular weight peroxides. Four peroxides of varying molecular weights and aromatic character have been synthesized. The effectiveness of these additives has been tested on a variety of aromatic polymers.

alpha

The crosslinking effectiveness of a high molecular weight carbene precursor, 4,4'-Bis(α-diazobenzyl)diphenyl ether, has been tested with both model compounds and aromatic polymers.

FOREWORD

This report was prepared by the Department of Chemistry at the University of Iowa, Iowa City, on Air Force Contract No. F33615-71-C-1139, initiated under Project 7342 "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials." It was administered under the direction of Air Force Materials Laboratory, Dr. F. L. Hedberg, AFML/MBP, as Project Scientist.

This report covers work from 1 April 1974 to 31 March 1975. It was submitted by the authors in April 1975.

The work which is reported herein was performed by J. K. Stille, K. Iwata, S. Norris and J. Wolfe.

Previous reports published under this contract (AFML-TR-70-5, Parts III-V) were concerned with the preparation of thermally stable, aromatic heterocyclic polymers.

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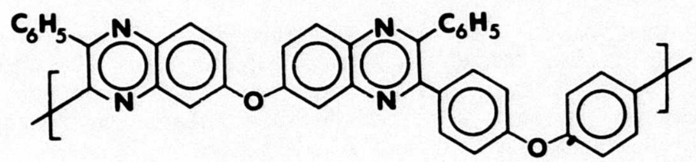
Crosslinking Systems for Aromatic Heterocyclic Polymers

I. Introduction

Research on high temperature polymers over the past ten years has produced a variety of new aromatic heterocyclic polymers based on the quinoxaline, anthrazoline, isoanthrazoline and quinoline ring systems. These polymers possess good thermooxidative stability and thus are good candidates for resins to be used in structural composites having high-temperature requirements. The major structural modifications of the heterocyclic polymer backbone which improve the solubility and processibility of these polymers are the addition of pendant phenyl groups and the introduction of flexible linkages, such as ether, sulfoxide, sulfone and meta- and ortho-phenylene groups, into the polymer backbone. In general, these structural modifications give the polymer a relatively low softening temperature which aids in fabrication; however, these modifications restrict the structural use-temperature to a value well below the thermal capabilities of the system. For example, the polyphenyl quinoxaline (1) has a Tg of 268°, but thermal decomposition does not occur below 500°.[1]



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One modification which raises or eliminates polymer transitions responsible for softening is the production of network structures by introducing chain cross-links into the system. Thus, the purpose of this research is the development of a method for the crosslinking of known heterocyclic polymers to afford thermally stable network systems. This can be accomplished by the thermally induced reaction of a dispersed reactive intermediate with the aromatic nuclei in the polymer to form thermally stable bonds and thus a thermally stable cross-linked network. A universal crosslinking additive is sought for aromatic and aromatic heterocyclic polymers. The additive can be dispersed in the polymer at some stage before processing, and then thermally processed to crosslink the fabricated polymer. The ideal additive should meet the following requirements: 1) Produce a reactive intermediate between 150-250° or lower. 2) Produce a reactive intermediate which will react with aromatic nuclei such that a thermally stable cross-link will be formed. 3) Produce a reactive intermediate without excessive generation of highly volatile materials. 4) Have

a high enough molecular weight such that it, its fragments or by-products will not come out of the polymer throughout the curing process. 5) Be compatible with the polymer such that it will be molecularly dispersed throughout. 6) Have some solubility in common organic solvents and be stable enough at room temperature to be shipped and handled safely.

II. Results and Discussion

A. Polymers for Crosslinking

Several samples including phenylated polyquinoxalines, polyquinolines, a polyanthroline and a polyisoanthrazoline have been prepared as summarized in Table 1. The samples have been employed as polymers for the crosslinking studies.

1. Polyquinoxalines

Samples of two high molecular weight phenylated polyquinoxalines, poly[2,2'-(p,p'- oxydiphenylene)-6,6'-oxybis(3-phenylquinoxaline)] (1) and poly[2,2'-(p,p'-oxydiphenylene)-6,6'-di(3-phenylquinoxaline)] (2), have been prepared as outlined in Figure 1.

The monomers needed for the preparation of polymers 1 and 2 are all commercially available or readily synthesized.[2]

The polymerization reaction was carried out in a 1:1 m-cresol: xylene mixture. The initial concentration of monomers was 20%, however, dilution to 10% solid content was necessary in some polymerizations in order to prevent gel formation in the later stages of reaction. Physical properties for polymers 1 and 2 are given in Table 2.

2. Polyquinolines

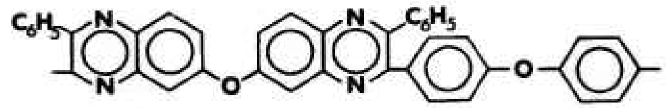
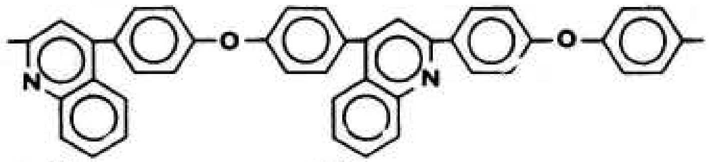
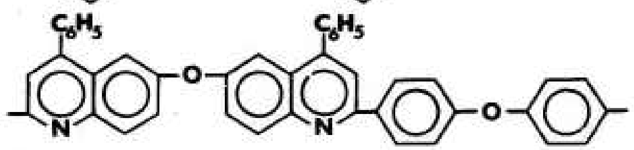
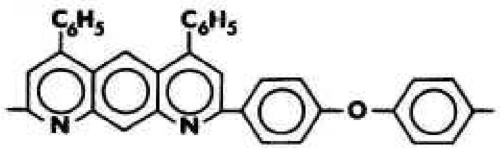
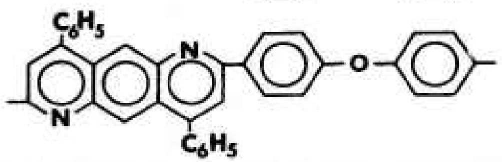
Poly[2,2'-(p,p'-oxydiphenylene)-4,4-p,p'-oxydiphenylene)-diquinoline] (3) and poly[2,2'-(p,p'-oxydiphenylene)-6,6'-oxybis(4-phenylquinoline)] (4) have been prepared. The preparation of 3 involves the acid catalyzed Friedländer reaction as outlined in Figure 2.

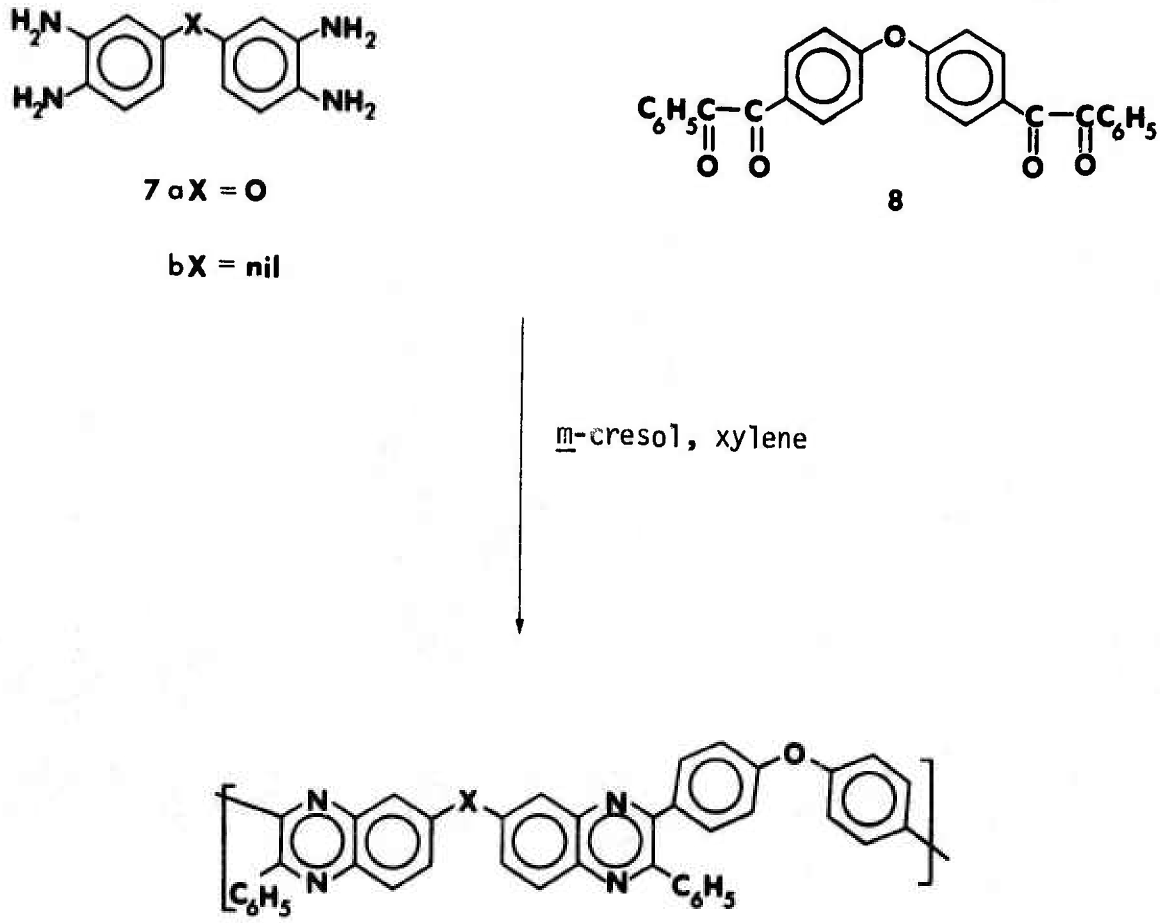
The preparation of polyquinoline-forming monomer 4,4'-bis(2-aminobenzoyl)diphenyl ether (9) has been described previously.[3] The synthesis has now been improved to give good yields in all steps, including a high yield of 9 in the Hofmann rearrangement. The synthetic scheme is outlined in Figure 3.

The diketo-diacid precursor, 4,4'-bis(2-carboxybenzoyl)diphenyl ether (10), has been prepared in large quantities by the two step synthesis, via the monoadduct 11, in an overall yield of 54%. However, the diketo-diacid 10 is more readily prepared in good yield by the one-step addition of two moles of phthalic anhydride to diphenyl ether. The success of the one-step synthesis results from the use of excess

Table 1

Aromatic Heterocyclic Polymers

Name		Structure
Polyquinoxaline		
Poly[2,2'-(p,p'-oxydiphenylene)-6,6'-oxybis(3-phenylquinoxaline)]	1	
Poly[2,2'-(p,p'-oxydiphenylene)-6,6'-di(3-phenylquinoxaline)]	2	
Polyquinoline		
Poly 2,2'-(p,p'-oxydiphenylene)-[4,4'-(p,p'-oxydiphenylene)-diquinoline]	3	
Poly 2,2'-(p,p'-oxydiphenylene)-[6,6'-oxybis(4-phenylquinoline)]	4	
Polyanthrazoline		
Poly[4,6-diphenyl-2,8-(p,p'-oxydiphenylene)-1,9-anthrazoline]	5	
Polyisoanthrazoline		
Poly[4,9-diphenyl-2,7-(p,p'-oxydiphenylene)-1,6-anthrazoline]	6	



1 X = O

2 X = nil

Figure 1

Synthesis of Polyquinoxalines

Table 2

Physical Properties of Polyquinoxalines

	Polymer 1	Polymer 2
TGA (film)		
Air: Break	560°C	550°C
N_2 : Break	560°C	560°C
: % wt loss at 800°	32	29
DSC, Tg	263°C	220°C
[η] m-cresol @ 25°	2.8	1.01

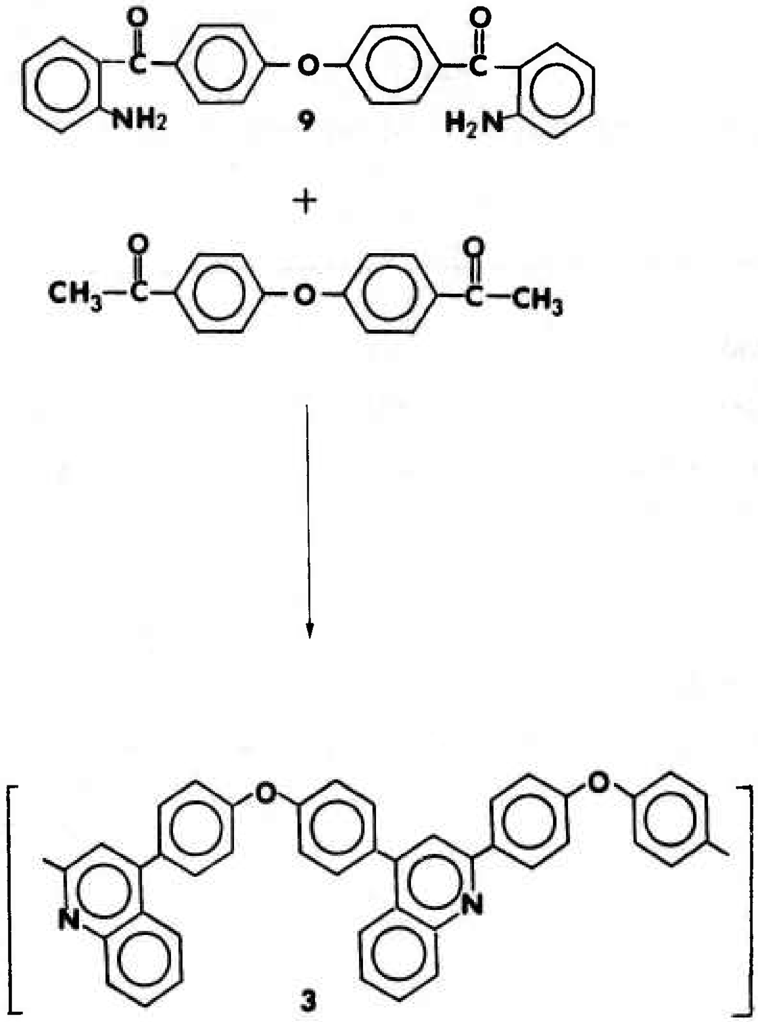


Figure 2

Synthesis of Poly[2,2'-(p,p'-oxydiphenylene)-4,4'-(p,p'-oxydiphenylene)diquinoline] (3)

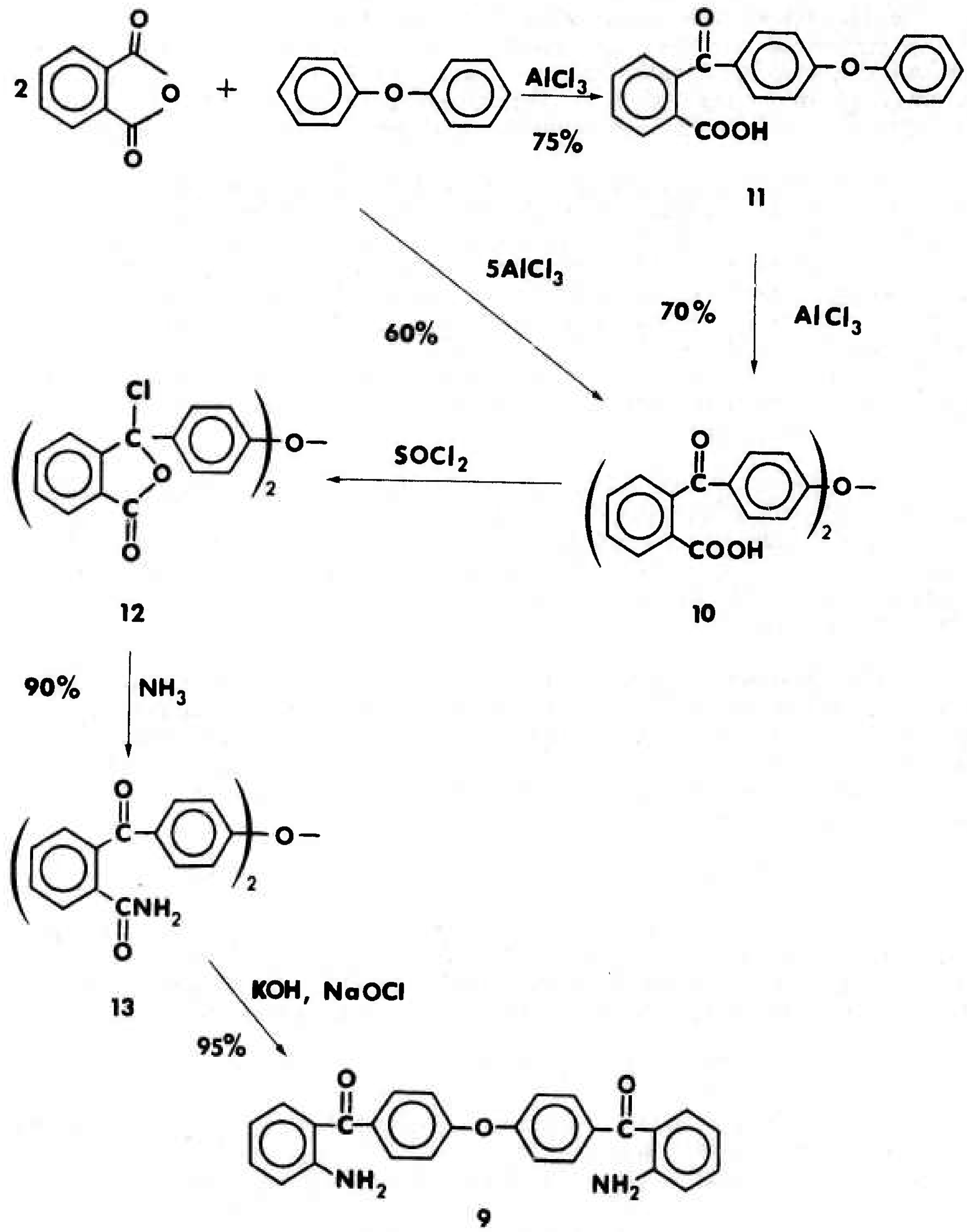


Figure 3

Synthesis of 4,4'-Bis(2-aminobenzoyl)diphenyl ether (9)

aluminum chloride and a more concentrated reaction medium than that used in the two-step preparation.

Treatment of the diacid 10 with excess thionyl chloride afforded the pseudo-acid chloride 12. Solution of 12 in dry N-methyl-2-pyrrolidone and treatment with gaseous ammonia at 0-10° gave the diketo-diamide 13 in a yield of 90%. This product is sufficiently pure to be used in the Hofmann rearrangement without further purification.

The Hofmann rearrangement is carried out in aqueous potassium hydroxide by the addition of a slight excess of sodium hypochlorite solution. Dissolution of the diamide is slow, but after heating the clear solution to 80°, the product precipitates as a bright yellow powder. The crude product, which shows only one carbonyl absorption at 1625 cm^{-1}, is obtained in 95% yield. Recrystallization from 95% ethanol affords bright yellow needles. The carbon-13 nmr spectrum of 9 is given in Table 3. The assignments given are based on the chemical shifts of related compounds, calculated values and off-resonance decoupling experiments.

The polymers 3 were prepared in a m-cresol-polyphosphoric acid solvent and ranged in viscosity from 0.18 to 0.57. The polymers were completely soluble in chloroform and m-cresol. Tan translucent films can be prepared from a 10% solution in chloroform or from a chloroform/m-cresol (1:1) mixture. These polymers have been employed as samples for crosslinking studies.

Polyquinoline 4 has been prepared from 4,4'-diacetyldiphenyl ether with 3,3'-dibenzoyl-4,4'-diaminodiphenyl ether in an analogous manner to the synthesis of polyquinoline 3. The inherent viscosity of the polymer was 0.94. The polymer was soluble in chloroform and gave translucent films. This polymer has also been employed as a sample for crosslinking studies.

3. Polyanthrazoline (5) and Polyisoanthrazoline (6)

Poly[4,6-diphenyl-2,8-(p,p'-oxydiphenylene)-1,9-anthrazoline] (5) and poly[4,9-diphenyl-2,7-(p,p'-oxydiphenylene)-1,6-anthrazoline] (6) have been prepared as reported earlier.[4] Mechanical properties of 5 and 6 are shown in Figures 4-7 and summarized in Table 4.

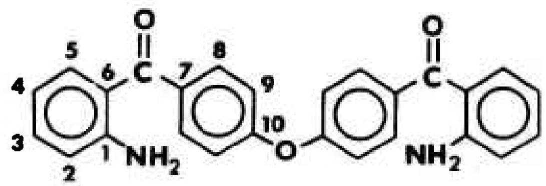
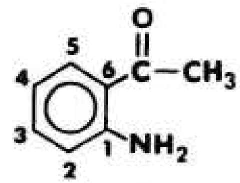
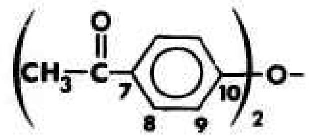
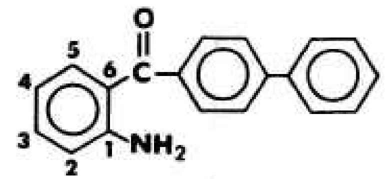
4. The Preparation of Model Compounds

As the model compounds of 2, 5 and 6, 2,3-diphenylquinoxaline (14), 2,4,6,8-tetraphenyl-1,9-anthrazoline (15) and 2,4,7,9-tetraphenyl-1,6-anthrazoline (16) have been prepared as outlined in Figure 8.

These compounds have been employed as models for the investigation of the reactivity of the crosslinking agents with corresponding heterocyclic polymers.

Table 3

^{13}C-nmr Spectrum of 4,4'-Bis(2-aminobenzoyl)diphenyl ether (9) and related compounds

						
Carbon	Off-Res	Observed*	Calc'd			
C=C	s	197.56	--	200.72	196.40	198.56
10	s	158.94	163.6	--	160.15	--
1	s	150.82	148.2	150.77	--	150.92
7	s	135.42	132.2	--	133.07	--
3	d	134.07	133.0	134.37	--	134.42
5	d	131.56	131.1	132.10	--	134.21
8			131.2	--	130.75	--
9	d	118.35	113.9	--	118.72	--
6	s	118.13	124.6	117.97	--	118.24
4	d	117.05	118.5	117.26	--	117.05
2	d	115.40	115.2	115.43	--	115.49

* In ppm downfield from TMS

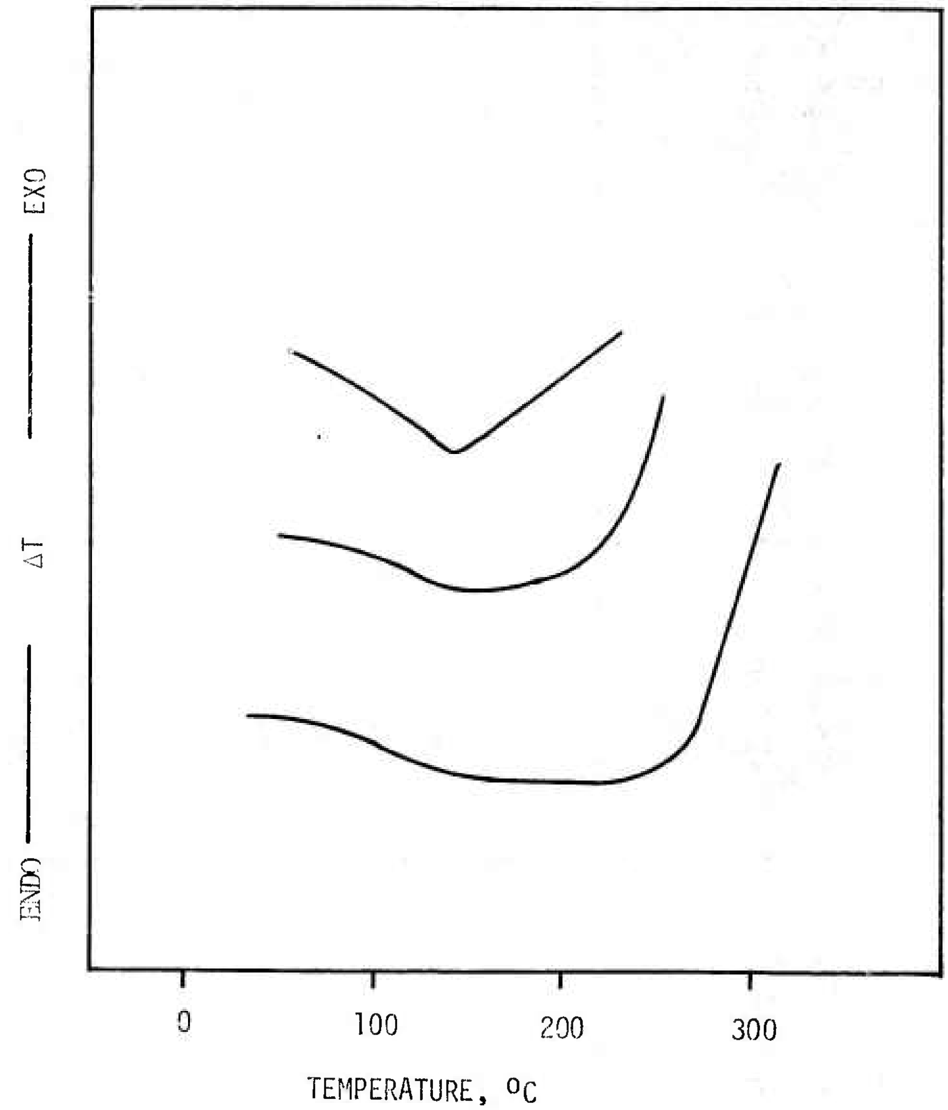


Figure 4
DSC Scan of Powdered Sample of Polyanthrazoline 5 in Air
(Heating Rate: 20°/Min)

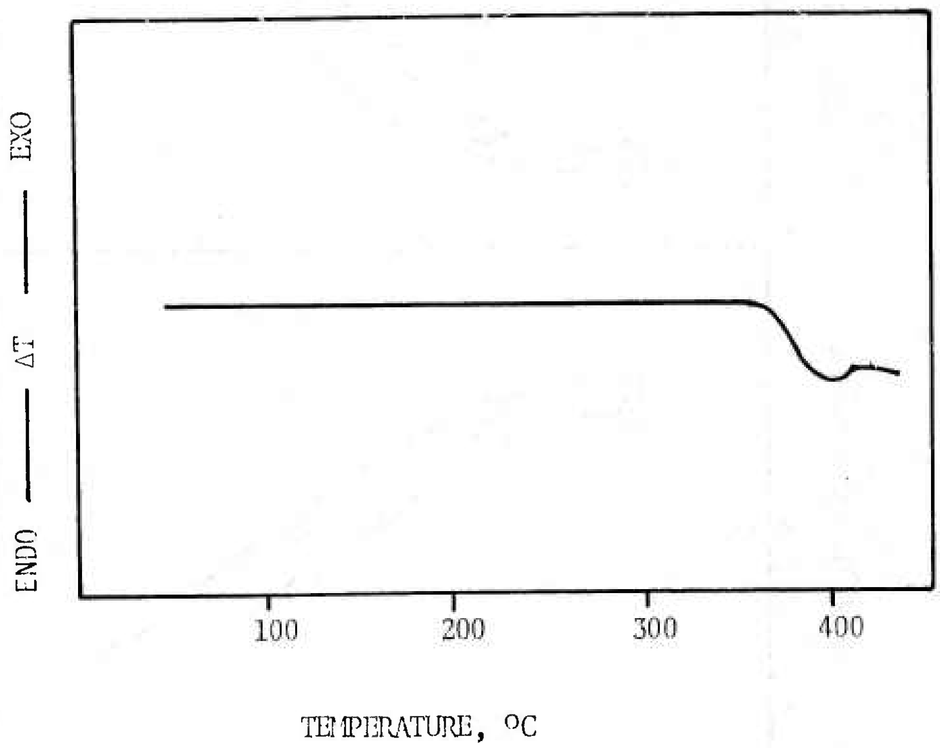


Figure 5

DSC Scan of Powdered Sample of Polyanthrazoline 5 in Nitrogen
(Heating Rate: 10°/Min)

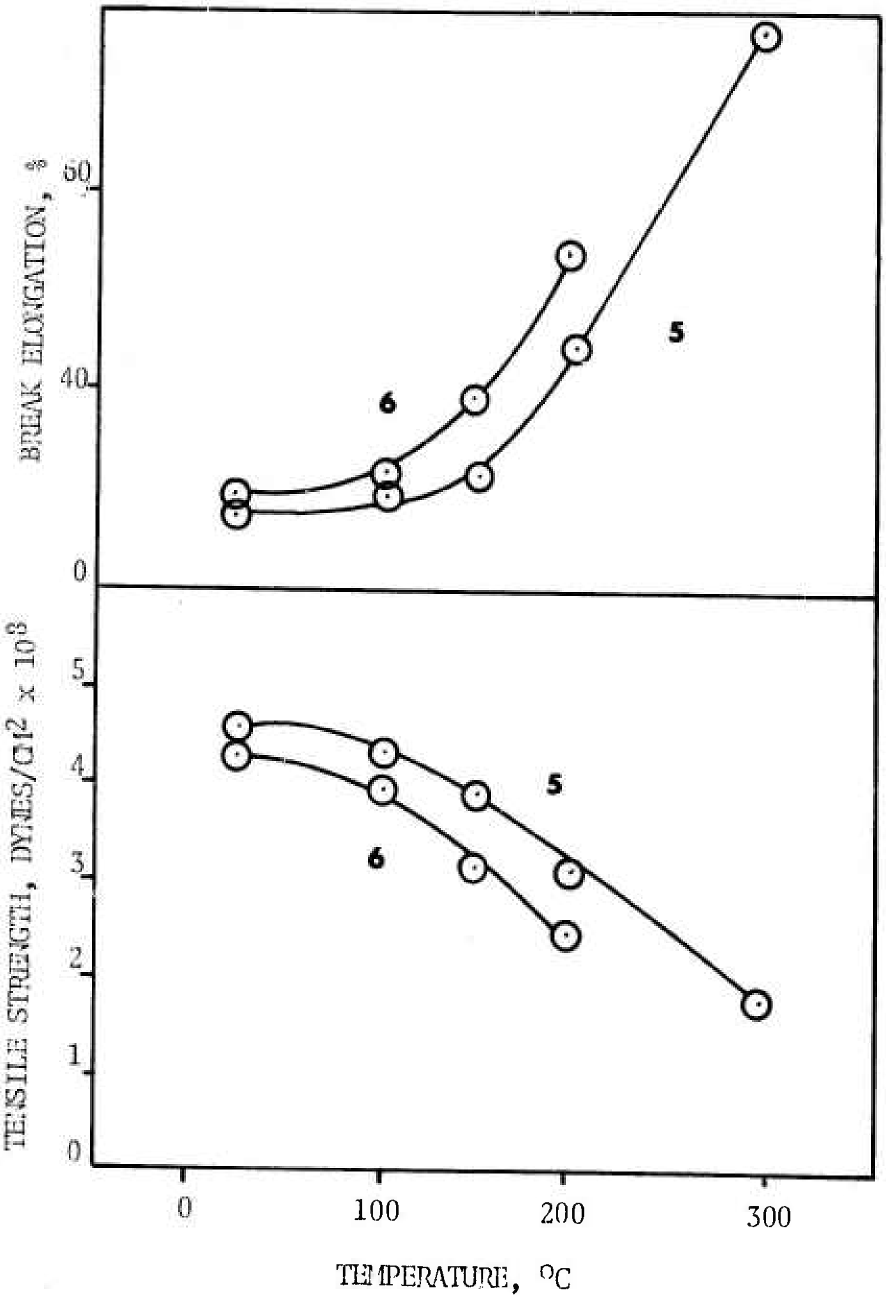


Figure 6
Mechanical Properties of Films of
of Polyanthrazoline 5 and Polyisoanthrazoline 6

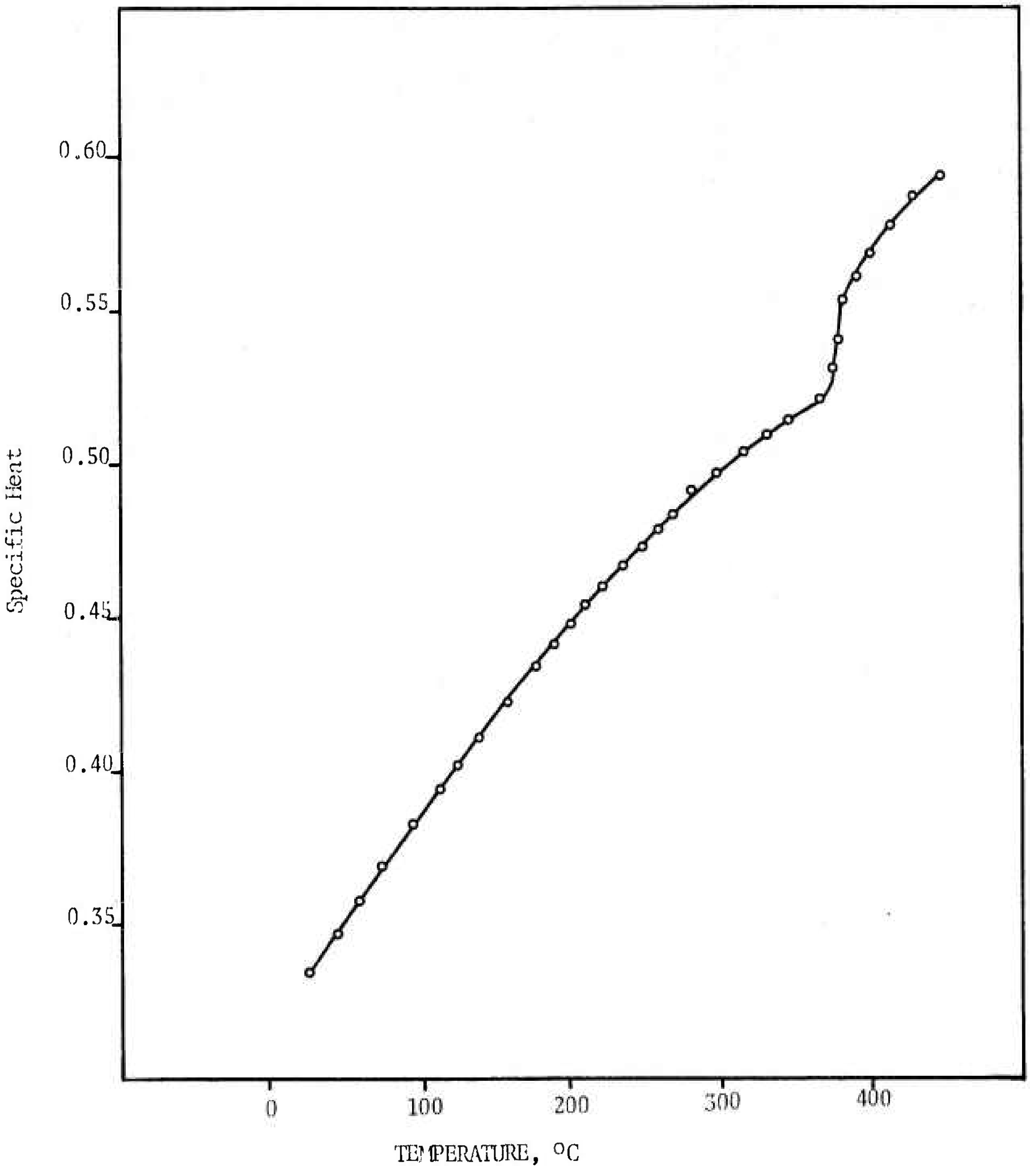
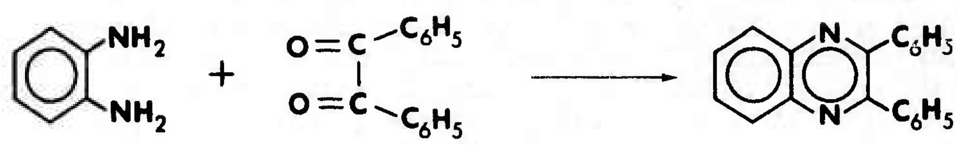


Figure 7
Specific Heat vs. Temperature for Polyanthrazoline 5

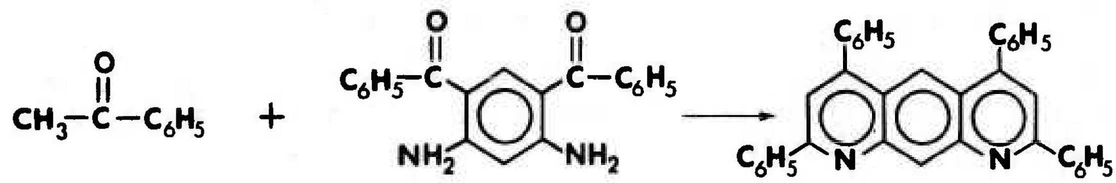
Table 4

Mechanical Properties of Polyanthrazoline 5 and Polyisoanthrazoline 6

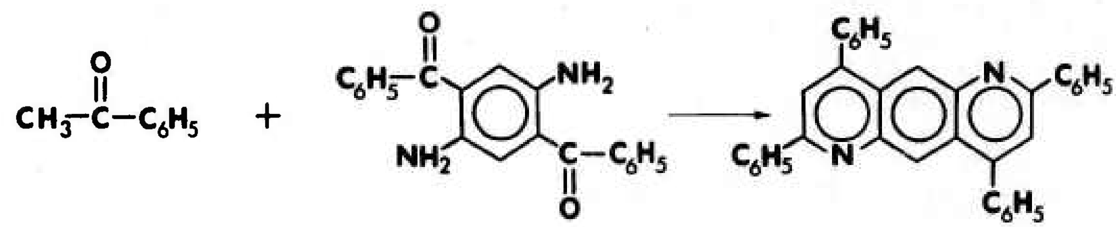
		Tg, °C			Tensile Str. (psi x 10^{-3})		Young's Mod, E',(psi)	
Polymer	η_{inh}	DSC	E"	Sp. Vol.	25°	200°	25°	450°
5	0.51	379	382	378	6.67	4.49	7.0×10^5	1.0×10^3
6	0.53	364	368	-	6.16	3.48	5.1×10^5	3.5×10^2



14



15



16

Figure 8
Preparation of Model Compounds

The compound 14 has been prepared by the analogous manner to the reported synthesis of 4,4'-di(2-quinoxalyl)diphenyl ether.[5]

The compounds 15 and 16 have been prepared by the analogous manner to the preparation of 5 and 6. Thus, 4,6-dibenzoyl-m-phenylenediamine or 2,5-dibenzoyl-p-phenylenediamine, and acetophenone were heated in polyphosphoric acid at 120° to obtain the model compounds in high yields. Data for 14, 15 and 16 are listed in Table 5.

B. Peroxides as Crosslinking Additives

There is little information available concerning the reaction of a peroxy radical with an aromatic ring. Although cumyl hydroperoxide will decompose and abstract hydrogen from hydrocarbon solvents and at the benzylic position of alkyl aromatics,[6] the direct reaction of this radical with aromatic nuclei has not been investigated. The hydroxy radical obtained from hydrogen peroxide does react with benzene, however, to produce biphenyl.[7]

$$2\ HO\cdot + C_6H_6 \longrightarrow C_6H_5\text{-}C_6H_5 + 2H_2O$$

In some preliminary tests in this laboratory, a film of a phenylated polyphenylene was partially crosslinked at 140° with benzoyl peroxide which was present in the polymer solution (benzene solvent) when the film was cast. A clear, partially insoluble crosslinked film without bubbles was obtained.

These preliminary results stimulated us to investigate peroxides as potential crosslinking additives.

1. Triphenylmethyl Peroxide (17)

Investigation into the use of peroxide additives as crosslinking agents for aromatic polymers involves the synthesis of high molecular weight peroxides. One such peroxide, triphenylmethyl peroxide (17), has been prepared in an overall yield of 40% by the reported synthesis[8] shown in Figure 9. The peroxide 17 decomposes at its melting point (177-178°). This decomposition occurs between 180-200° as shown by differential scanning calorimetry (DSC) (Figure 10).

A film of polymer 2 containing 5 wt % of peroxide 17 was cast from a chloroform solution containing 15% solids. Since 17 is insoluble in aromatic solvents and is only slightly soluble in chloroform, an excess of chloroform was added to totally dissolve 17 in the polymer solution. The excess solvent was then removed under reduced pressure at room temperature. Films were cast and air dried. However, as the solvent evaporated, crystals of the peroxide formed, affording a film containing crystals of the additive instead of a molecularly dispersed sample. The DSC of the polymer film (Figure 11) indicates the decomposition temperature of 17 in the polymer structure is essentially the

Table 5

Physical Properties of Model Compounds 14, 15 and 16

Compd.	mp (°C)	Anal.		C	H	N	MS m/e
14	125-126	$C_{20}H_{14}N_2$	Calcd	85.08	5.00	9.92	282, 281, 178, 153, 104, 77
		(M.W. 282.35)	Found	84.95	4.95	9.91	
15	254-263	$C_{36}H_{24}N_2$	Calcd	89.22	4.99	5.78	486, 485, 484, 4-7. 301, 277, 242
		(484.60)	Found	89.98	5.18	5.84	
16	375-378	$C_{36}H_{24}N_2$	Calcd	89.22	4.99	5.78	486, 485, 484, 400, 301, 277, 242
		(484.60)	Found	89.07	5.10	5.83	

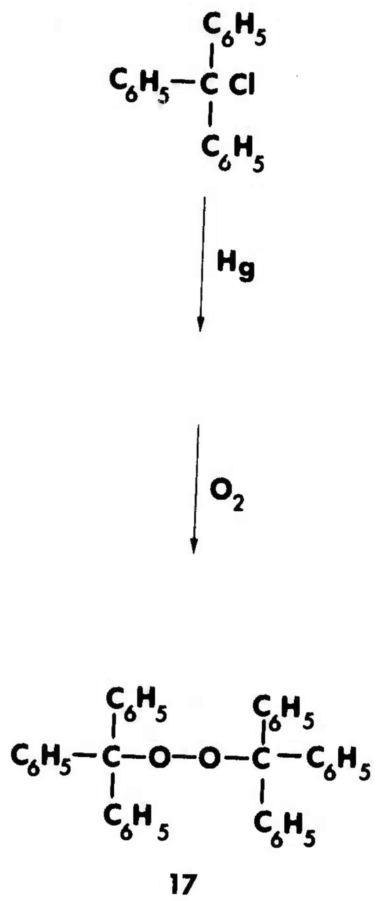


Figure 9

Synthesis of Triphenylmethyl Peroxide (17)

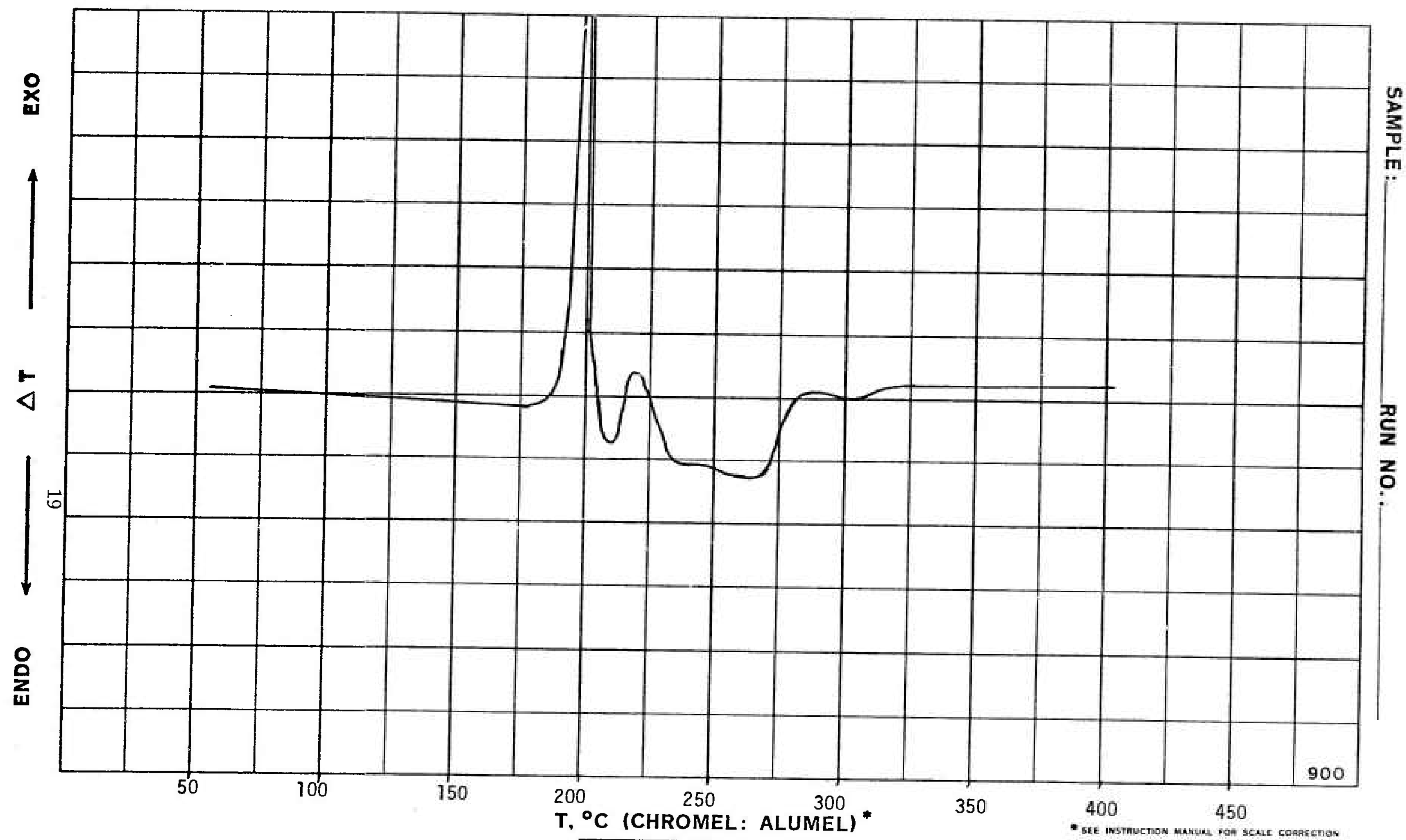


Figure 10

DSC of Triphenylmethyl Peroxide (17)

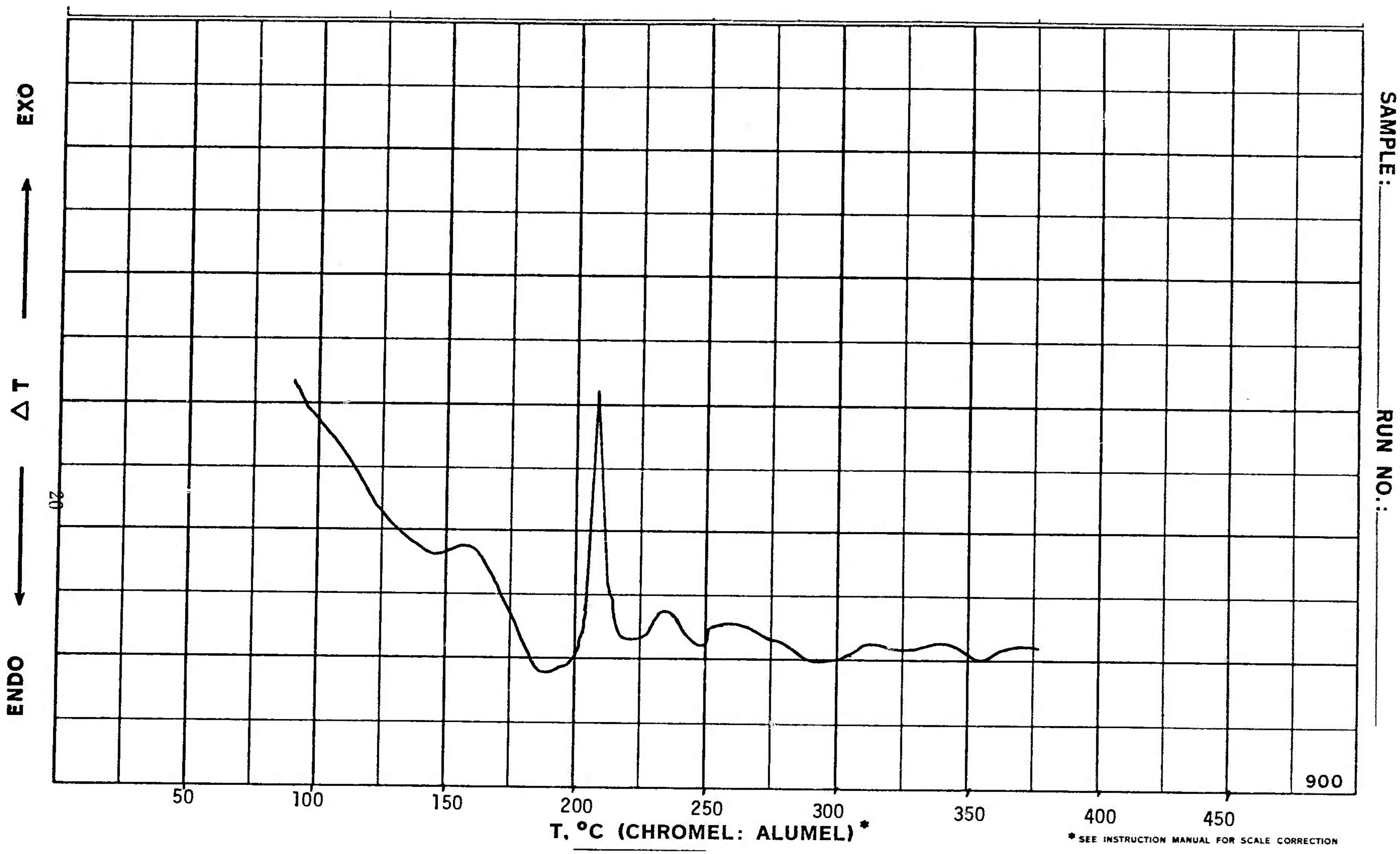


Figure 11

DSC of Film of Polymer 2 before Cure

same as in a neat sample.

Thermal crosslinking of this polymer film was carried out by heating the film at 225-230° under a high vacuum (<0.01 torr) for 3.5 hr. A comparison of the DSC traces of the cured film (Figure 12) with the starting polymer 2 show the transition is present in both polymers, but is not as distinct in the cured film. The sample is still readily soluble in chloroform, indicating the absence of a network structure.

2. Benzoyl Peroxide (18)

The effectiveness of peroxide additives as reagents for crosslinking aromatic polymers was investigated by thermally curing a film of polyquinoxaline (2) with commercially available benzoyl peroxide (18). A film of polymer 2 containing 6.5% of 18 was cast from a chloroform solution. The benzoyl peroxide was completely compatible with the polymer, thus resulting in a clear, uniform film. The film was then thermally cured in an oven at a temperature of 115°-125° for 2 hr. The resulting film was still clear and uniform, but retained complete solubility in chloroform. Differential scanning calorimetry (DSC) does indicate, however, that the glass transition temperature of the cured polymer (275°) is higher than the uncured polymer (225°) (see Figure 13). This increase in glass transition temperature suggests that some degree of crosslinking occurred, but the complete solubility of the cured polymer indicates the absence of a network structure.

3. Attempted Synthesis of 4,4'-Bis(triphenylmethyl peroxide) (19)

a. The ineffectiveness of benzoyl peroxide as a crosslinking agent may be attributed to the necessity for the formation and collision of two free radical sites on the polymer backbone. Since the polymer chain is relatively rigid, the free radicals formed on the chain may remain isolated from each other. However, a crosslinking agent capable of forming two free radical sites per molecule should be more effective in forming a crosslinked network. Thus, the synthesis of a bisperoxide 19 as shown in Figure 14 has been investigated.

The synthesis involved the acylation of diphenyl ether which afforded 4,4'-dibenzoyldiphenyl ether (20) in a yield of 72.5% after recrystallization. Treatment of 20 with phenylmagnesium bromide and then anhydrous hydrogen chloride gas afforded the dichloride 21 in a 60.9% yield. Reduction of 21 with zinc in glacial acetic acid afforded an 82.9% yield of the known alkane 22.[9]

The final step of the proposed synthesis of the bis-peroxide 19 has been carried out in a manner analogous to the reported synthesis of other mixed peroxides.[10] However, treatment of the bisalkane 22 with a 25% excess of triphenylmethyl hydroperoxide in the presence of

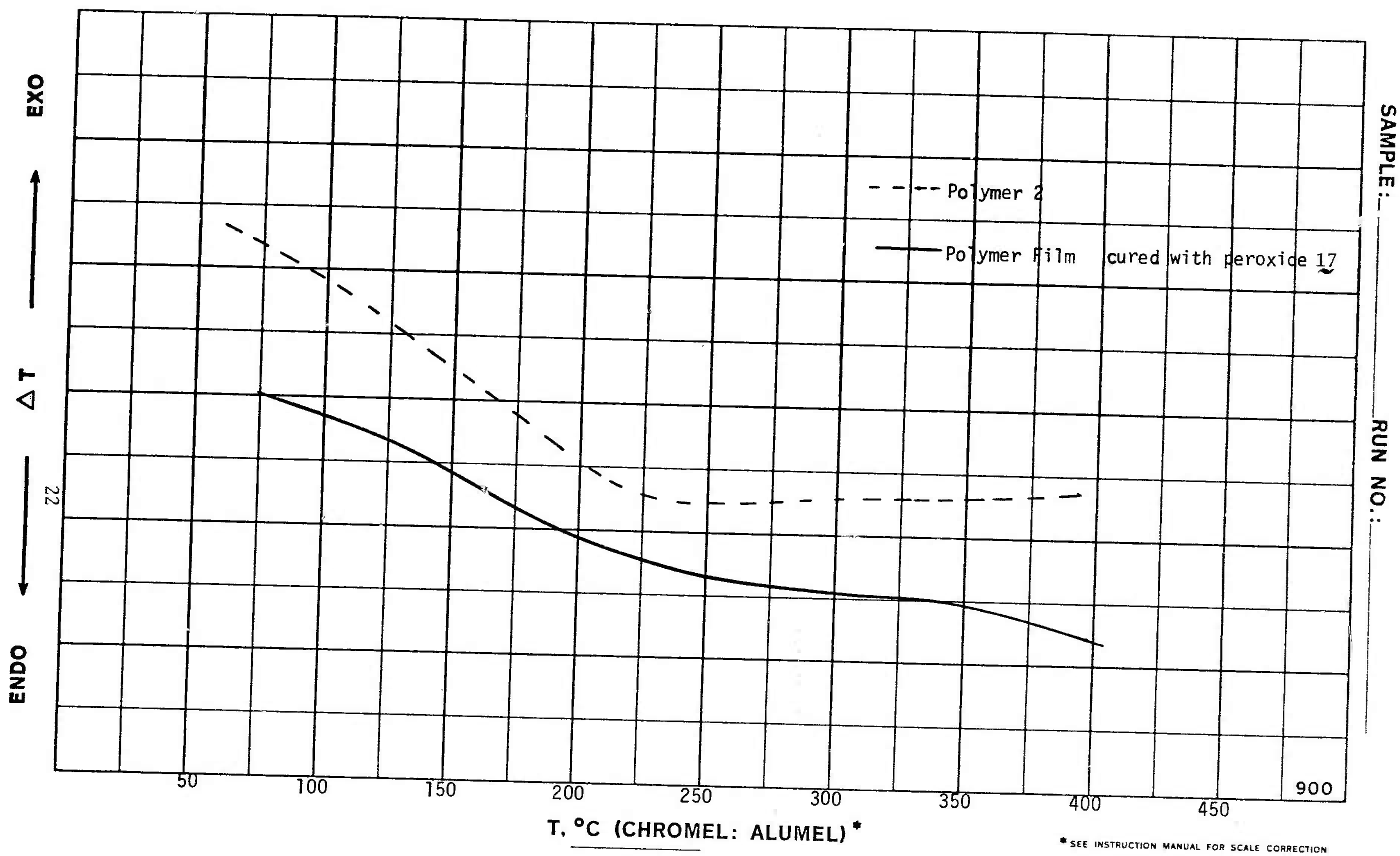


Figure 12

Comparison of DSC of Polymer 2 and Polymer Film Cured with Peroxide (17)

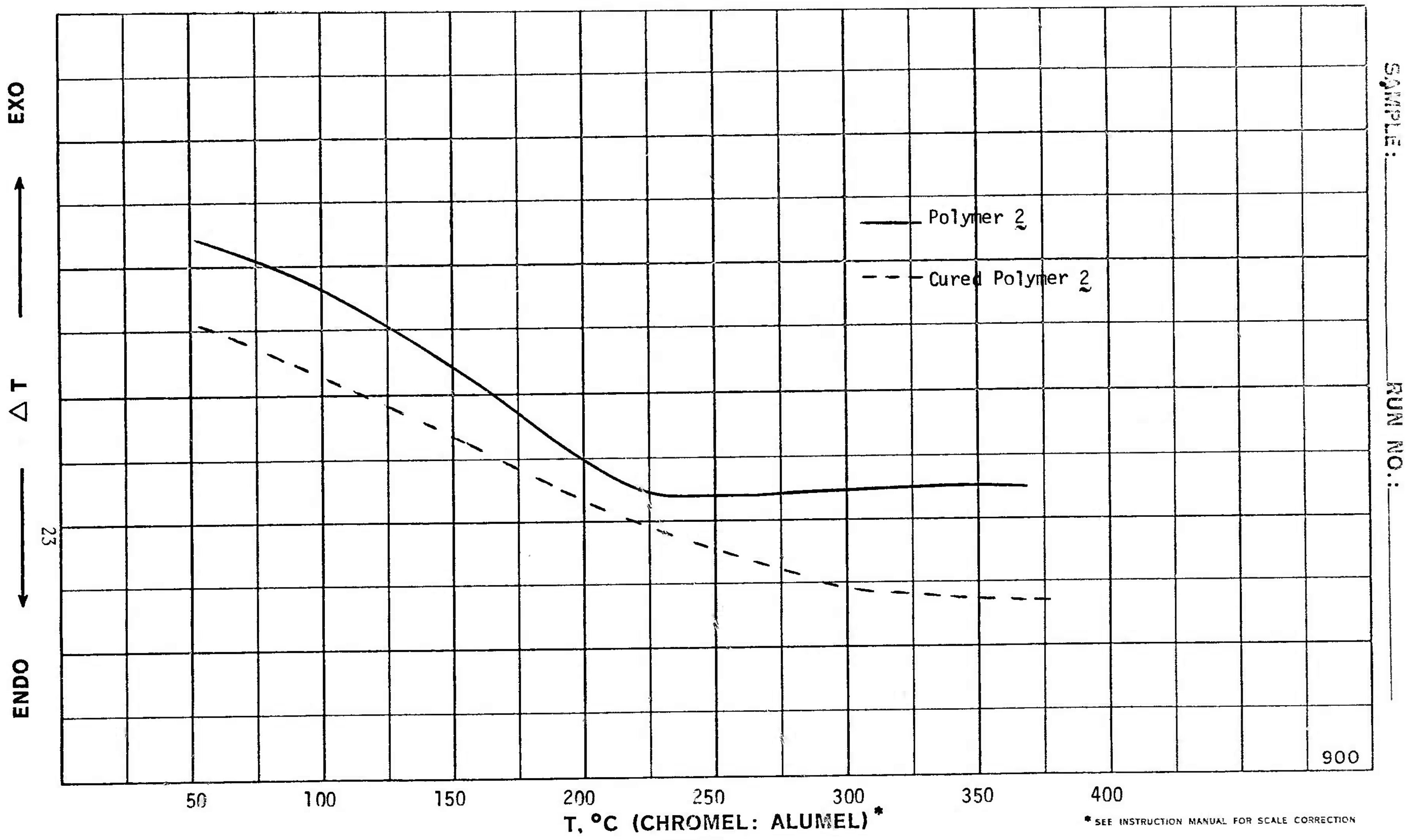


Figure 13

DSC of Cured and Uncured Polymer 2

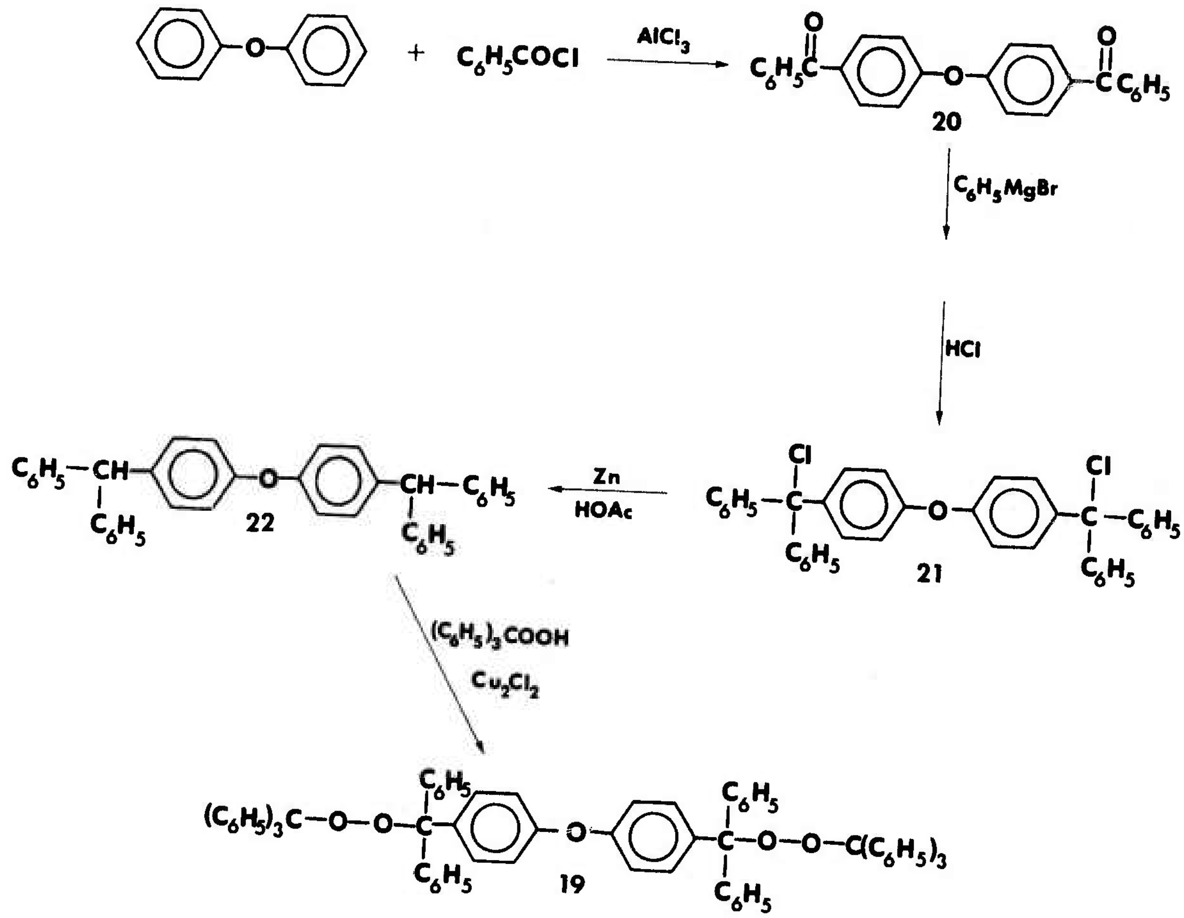


Figure 14

Synthesis of 4,4'-Oxybis(triphenylmethyl peroxide) (19)

cuprous chloride as a catalyst afforded a red-brown oily product. The product showed infrared absorptions at 1600, 1490, 1650, 1235, 1220 (shoulder), 750 and 690 cm^{-1}. In addition to these bands, the product showed an absorption at 1660 cm^{-1}, characteristic of aromatic ketones. The characteristic feature of this reaction is that unexpected triphenylmethyl peroxide was isolated as a by-product in a 41% yield. On the other hand, it is reported[10] that alcohols from the corresponding hydroperoxides are formed as by-products.

The proposed synthesis of the bis-peroxide 19 has been carried out in various reaction conditions. Cuprous chloride and manganous chloride were used as catalysts. Ethyl acetate, benzene and acetic acid were used as solvents. The reaction conditions and the results are summarized in Table 6. In all experiments attempted, however, bisalkane 22 was recovered in 43-87% yields and the expected product 19 was not obtained. Triphenylmethyl hydroperoxide did not take part in the reaction with bisalkane 22. Under mild conditions such as ethyl acetate or benzene, unexpected triphenylmethyl peroxide was isolated as a by-product. In the reaction in acetic acid, triphenylmethyl alcohol was isolated. All of the reactions gave a red-brown oily product which showed infrared absorptions characteristic of benzophenone. It has been assumed that a portion of the triphenylmethyl hydroperoxide was converted into benzophenone.

These experiments suggest that the reactivity of triphenylmethyl hydroperoxide is different from that of trialkylmethyl hydroperoxides such as tert-butyl hydroperoxide.[10]

b. Additional routes have been investigated in efforts to obtain bisperoxide 19. The synthetic schemes are outlined in Figure 15.

The proposed synthesis of the bis-peroxide 19 has been carried out in a manner analogous to the reported synthesis of dicumyl peroxide[11] and the modification of the reported synthesis of triphenylmethyl hydroperoxide.[12] 4,4'-Bis(diphenyl hydroxymethyl)diphenyl ether (24) has been prepared by the modification of the reported synthesis of bis-chloride. The bis-alcohol 24 and a two-fold molar amount of triphenylmethyl hydroperoxide were treated with perchloric acid, in the presence of magnesium sulfate as a dehydrating agent, in benzene and dioxane. It was observed by TLC analysis that the reactants were recovered.

In addition, triphenylmethyl alcohol and triphenylmethyl peroxide were isolated and identified by comparison with authentic samples.

The low reactivity of 24 might be due to the reduced electrophilicity of the carbonium ion formed from 24, because of the delocalization of the positive charge to the phenyl groups.

The bis-chloride 21 was treated with triphenylmethyl hydroperoxide and triethylamine in tetrahydrofuran. However, the reactants were recovered.

Table 6

Reaction of 22 with triphenylmethyl hydroperoxide

Exp. No.	Reactants				Solvent	Reaction temp./time	Compounds isolated (g)			
	22 g(mmole)	$(C_6H_5)_3COOH$ g(mmole)	Catalyst	mg(mmole)	(ml)	(°C/hr)	22	a	b	c
1	2.0(4.0)	5.5(20)	Cu_2Cl_2	40(0.2)	Ethyl acetate(20)	65/22	0.86	2.1	-	4.3
2	1.0(2.0)	2.2(8.0)	"	16(0.08)	Benzene (10)	65/15	0.87	0.59	-	1.4
3	1.0(2.0)	2.2(8.0)	"	16(0.08)	Benzene (10)	80/48	0.71	-	-	2.7
4	0.50(1.0)	1.1(4.0)	"	16(0.08)	Benzene (10)	45/38	0.24	0.59[d]	-	0.84
5	1.0(2.0)	2.2(8.0)	$MnCl_2 \cdot 4H_2O$	8(0.04)	Acetic acid (3)	80/22	0.86	-	0.76	0.91

a. $(C_6H_5)_3COOC(C_6H_5)_3$

b. $(C_6H_5)_3COH$

c. oil

d. contaminated with 22.

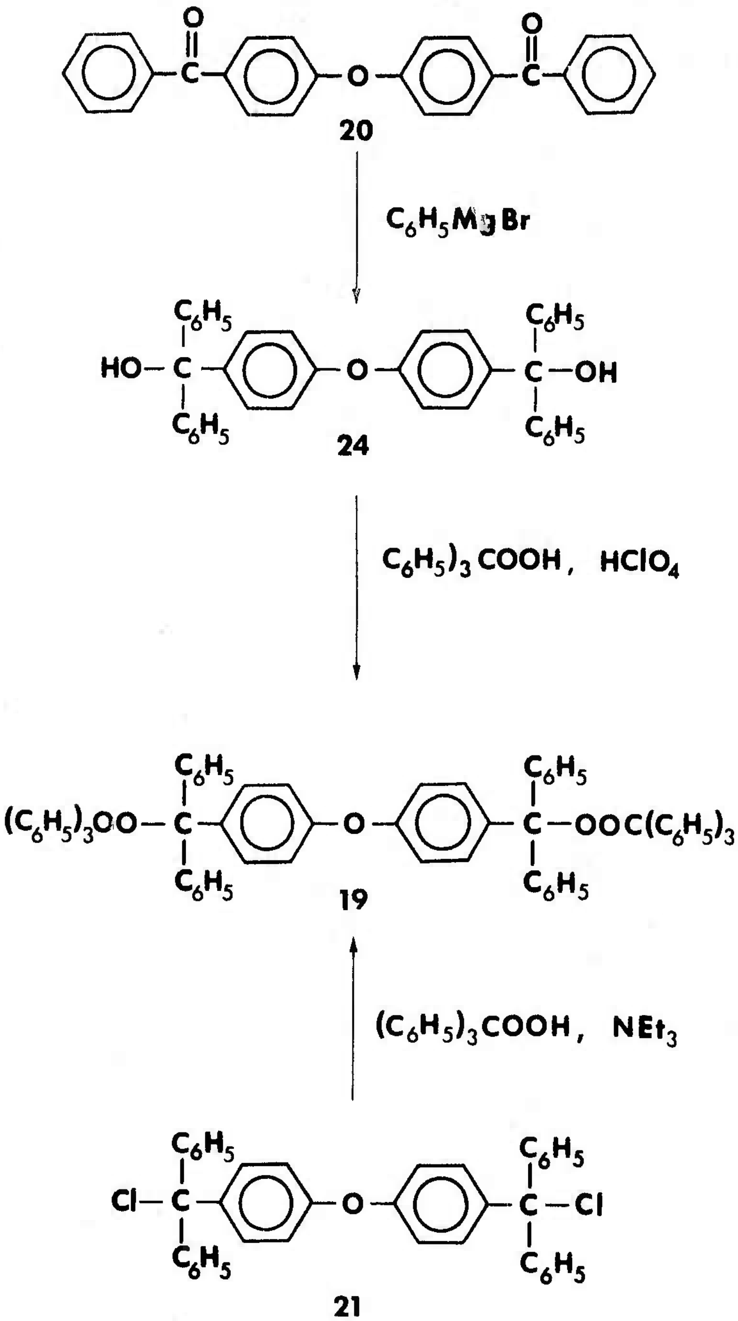


Figure 15

Synthetic Routes to 19

c. In this experiment, the synthesis of oxybis(triphenylmethyl peroxide) (19) from triphenylmethyl chloride and 4,4'-bis(diphenylchloromethyl)diphenyl ether (21) has been investigated. The synthetic route is shown in Figure 16. The reaction was carried out in a manner analogous to the reported synthesis of triphenylmethyl peroxide from triphenylmethyl chloride.[8] Thus, triphenylmethyl chloride and 4,4'-bis(diphenylchloromethyl)diphenyl ether was treated with mercury followed with air to obtain an orange colored benzene solution. The by-product of triphenylmethyl peroxide was removed by filtration. The residual benzene solution was fractionated by column chromatography by using a silica gel/benzene system to obtain a white powder. The product melted at 162-165°; ir=1610, 1500, 1455, 1250, 755 and 705 cm^{-1}. However, elemental analysis showed that the purified product was not the expected compound 19.

4. 4,4'-Oxybis(triphenylmethyl hydroperoxide) (25)

A convenient synthesis of 4,4'-oxybis(triphenylmethyl hydroperoxide) (25) has been found and is outlined in Figure 17. The synthesis of the bis-hydroperoxide 25 has carried out in a manner analogous to the reported synthesis of triphenylmethyl hydroperoxide.[12] The bis-chloride 21 was treated with 30% aqueous hydrogen peroxide in acetone using sodium hydroxide as an acid acceptor. The bis-hydroperoxide 25 was obtained in a 53% yield; mp. 129-130° (decomp.).

5. Polyperoxide (26)

Preliminary synthesis of polyperoxide 26 has been carried out in a manner analogous to the reported synthesis of triphenylmethyl peroxide[8] from triphenylmethyl chloride. The synthetic route is outlined in Figure 18. Thus, 4,4'-bis(diphenyl chloromethyl)-diphenyl ether (21) was treated with mercury followed with air to obtain polyperoxide (26) as a yellow powder. Although it has not yet been fully characterized, the following observations suggest that it is a low molecular weight oligomer terminated with a stable free radical of the trityl type: 1) The benzene solution of this compound shows the orange color characteristic of the trityl free radical; 2) The heat of decomposition of 26 is small compared to that of 25; 3) The ir and nmr spectra show no peaks which indicate the presence of HO-, HOO- and benzoyl group which is expected to be in the terminal group. The elemental analysis of 26 suggests that 26 is a low molecular weight oligomer terminated with a stable free radical of the trityl type.

6. Preparation and Curing of Films Containing 4,4'-Oxybis(triphenylmethyl hydroperoxide) (25) and Polyperoxide (26) and Preliminary Investigation by DSC

The effectiveness of the peroxides of 25 and 26 as crosslinking agents of polyquinoxaline has received preliminary investigation. Poly[2,2'-(p,p'-oxydiphenylene)-6,6'-di(3-phenylquinoxaline)] (2) was

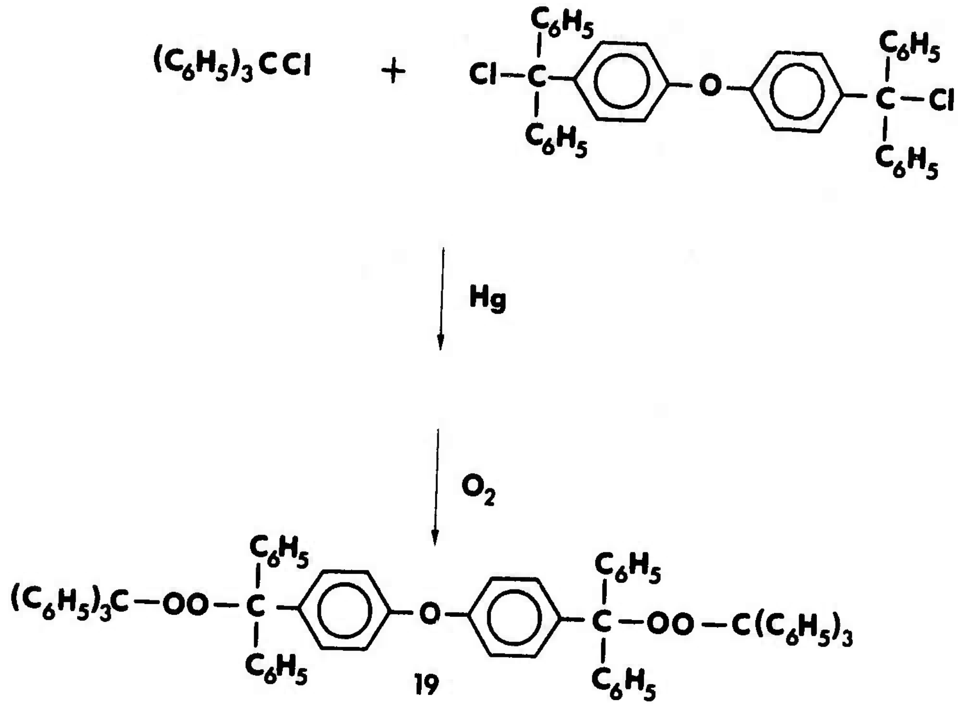


Figure 16
Proposed Synthesis of 4,4'-
Oxybis(triphenylmethyl peroxide) (19)

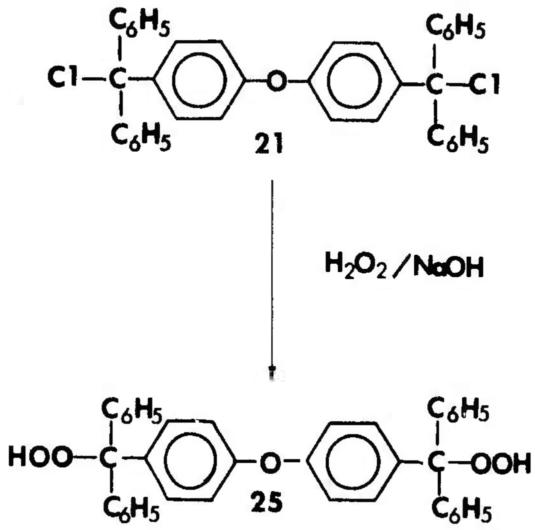


Figure 17

Synthesis of 4,4'-Oxybis(triphenylmethyl hydroperoxide) (25)

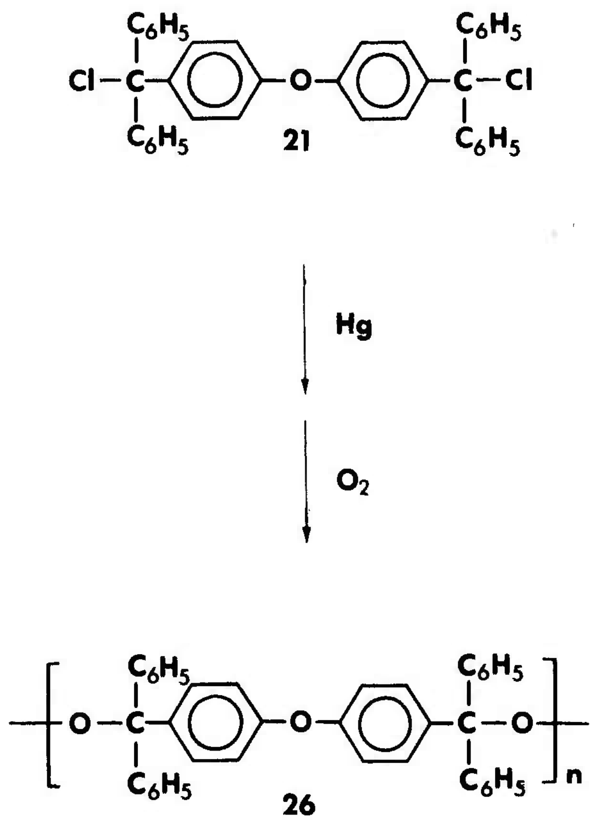


Figure 18
Synthesis of Polyperoxide 26

used as a polymer sample for this purpose.

The physical properties of crosslinking agents are shown in Table 7 together with those of triphenylmethyl peroxide. The DSC curves are given in Figure 19. All produce a reactive intermediate above 150° as shown by differential scanning calorimetry (DSC) measurements; all are compatible with polymer 2 such that they are molecularly dispersed throughout; all have good solubility in common organic solvents (such as chloroform) and are stable enough at room temperature to be shipped and handled safely.

Films of polyquinoxaline 2 including 25, 26 and triphenylmethyl peroxide were cast from chloroform solutions containing 10% solids. Films were cast and air dried. Thermal crosslinking of these polymer films was carried out by heating the films in a mercury bath under a nitrogen atmosphere. The conditions of the heat treatment and the results are given in Table 8. The DSC traces are shown in Figures 20-22.

Both of the films containing 25 and 26 were obtained as transparent tough films, indicating that these crosslinking agents have good compatibility with polymer 2 both before and after the heat treatment. Furthermore, the expected evolution of volatile material which is generated during the heat treatment did not have an undesirable influence upon the film. Presumedly, bubble formation was avoided because of the low concentration of the crosslinking agent.

As shown in Figure 20, the DSC of the polymer film Ib indicates the decomposition temperature of 25 in the polymer structure is essentially the same as in a neat sample.

Comparison of the DSC traces of the heat treated film (IIIa) of polymer 2 with nonheat-treated sample (IIIb) is given in Figure 22. No distinct transition could be observed in IIIb. On the other hand, a distinct and reproducible inflection which might be due to the glass transition appeared near 300° for sample IIIa. No distinct inflection could be observed in the films Ia and IIa even after the heat treatment.

All samples of the cured films are still readily soluble in chloroform, indicating the absence of a network structure.

In order to confirm the possibility of crosslinking, a model reaction between 2,3-diphenylquinoxaline (14) and triphenylmethyl hydroperoxide (23) has been performed. The reaction was carried out in bulk principally at the same condition as that used for the curing of the polyquinoxaline (2) film containing 4,4'-oxybis(triphenylmethyl hydroperoxide) (25). Thus, the mixture of equimolar amounts of 14 and 23 was heated for 2 hr each at 100°, 125°, 150°, 175° and 200°. Then, the reaction mixture was analyzed by mass spectroscopy. However no peak

Table 7

Physical Properties of Additives

Additive	mp (^{o}C)	Decomp. temp.[b] by DSC (^{o}C)	Compatibility with **2**	Solubility in $CHCl_3$
25	128-129	180	yes	yes
26	Amorphous	180	yes	yes
Triphenylmethyl peroxide	176-177	200[a]	no	yes

[a]lit. 5 b. Heating rate: $20^{o}C$/Min. in nitrogen

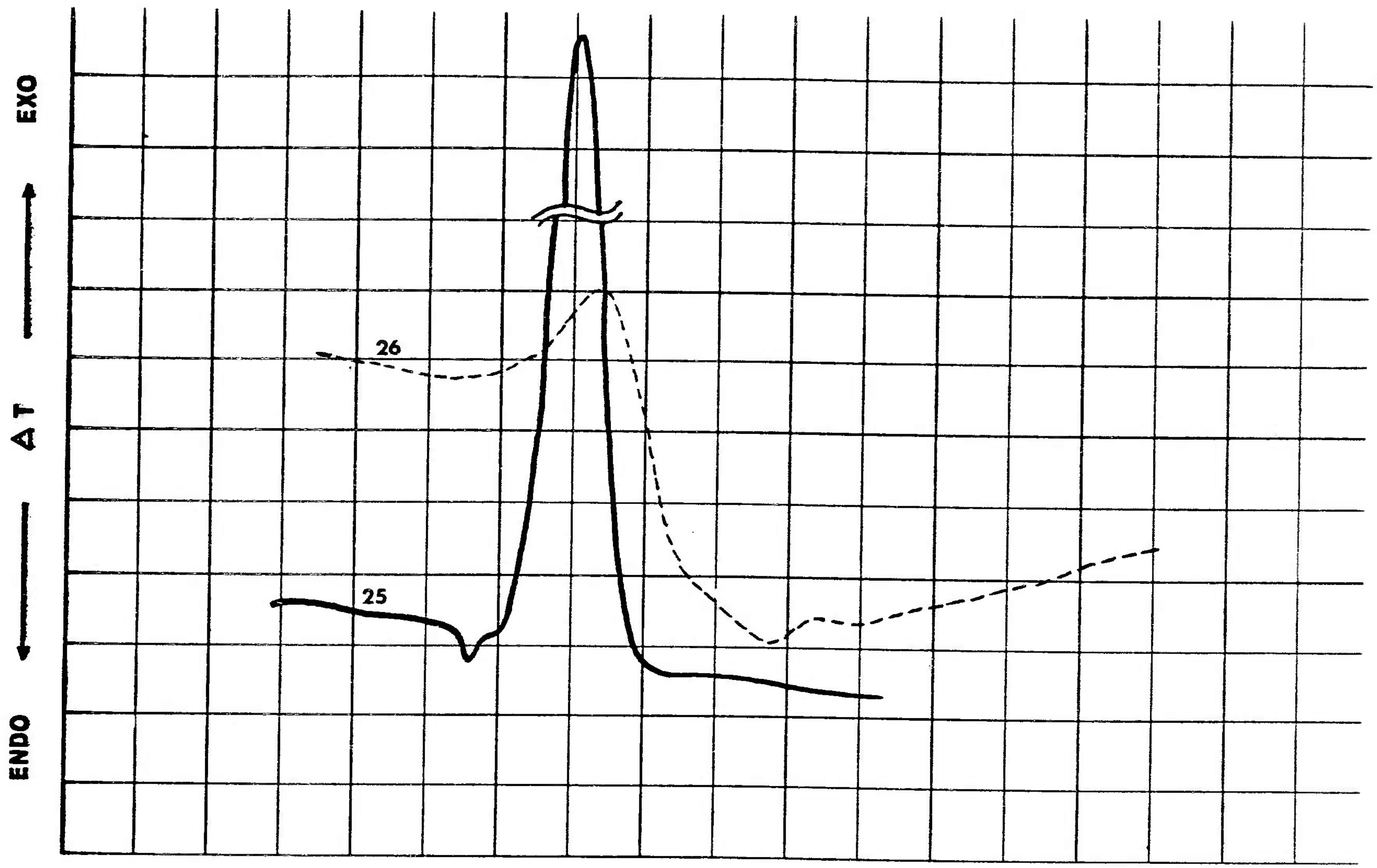


Figure 19
DSC Curves of Additives $\underset{\sim}{25}$ and $\underset{\sim}{26}$

Table 8

Polyquinoxaline 2 Film including Various Additives

No.	Film Composition (wt/wt)	Heat Treatment ($^{o}C/hr$)	Appearance	Solubility in $CHCl_3$
Ia	2/25 (100/5)	125/2, 150/2, 175/2, 200/2	yellow transparent	soluble
Ib	2/25 (100/5)	none	yellow transparent	soluble
IIa	2/26 (100/5)	125/2, 150/2, 175/2, 200/2	yellow transparent	soluble
IIb	2/26 (100/5)	none	yellow transparent	soluble
IIIa	2	125/2, 150/2, 175/2, 200/2	yellow transparent	soluble
IIIb	2	none	yellow transparent	soluble

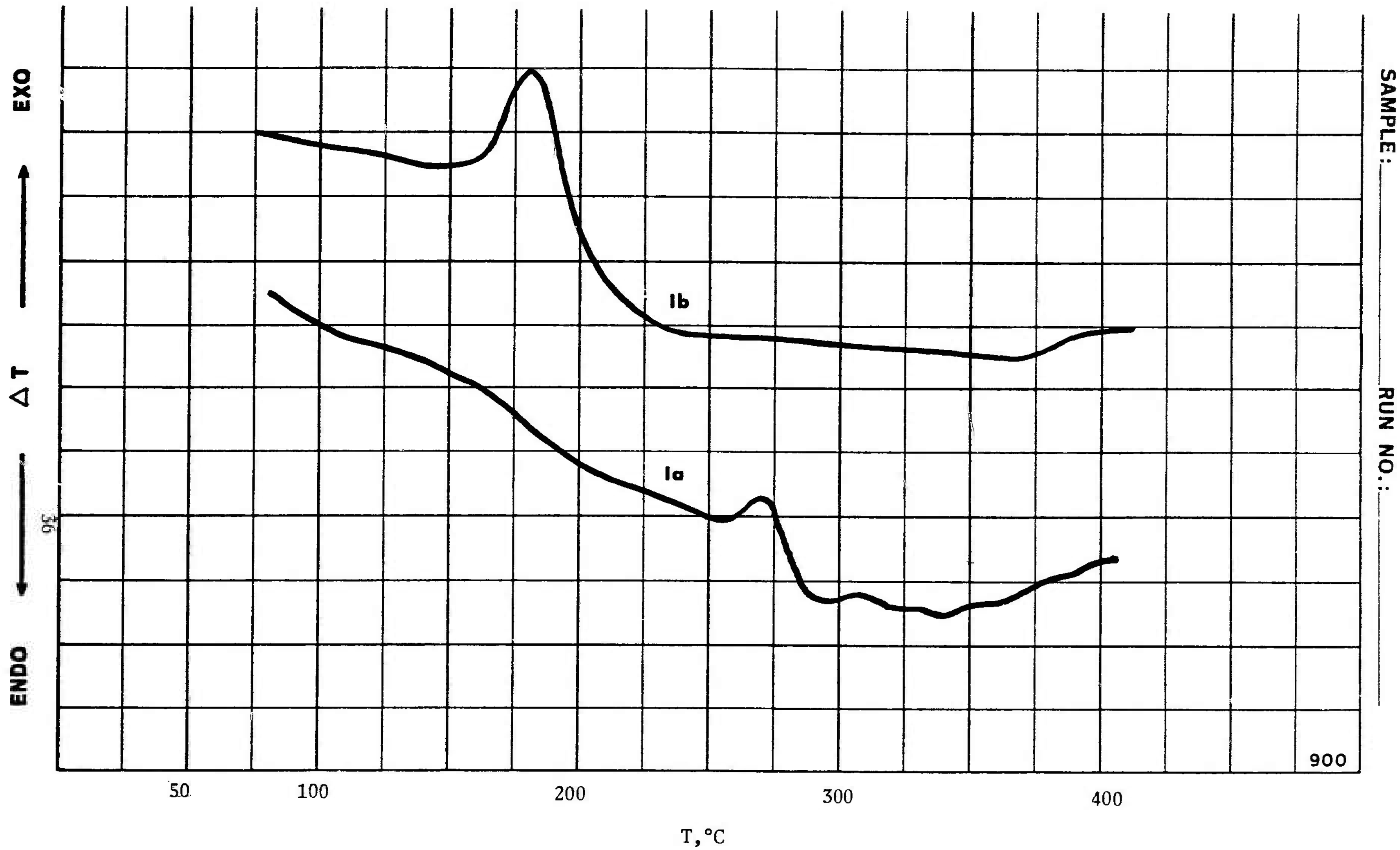


Figure 20

DSC Curves of Polymer Films Ia and Ib

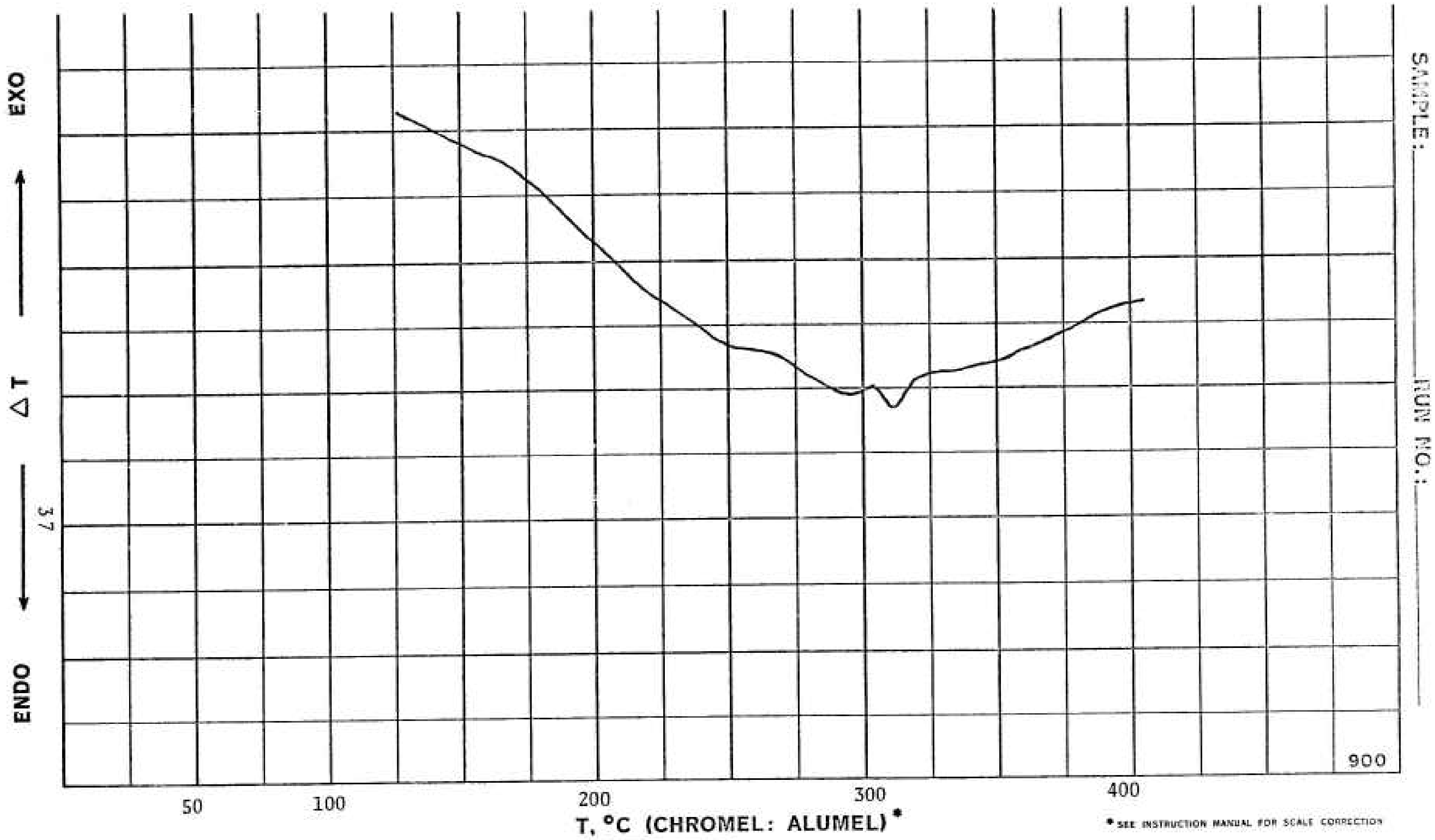


Figure 21

DSC Curve of Polyquinoxaline 2 including 25

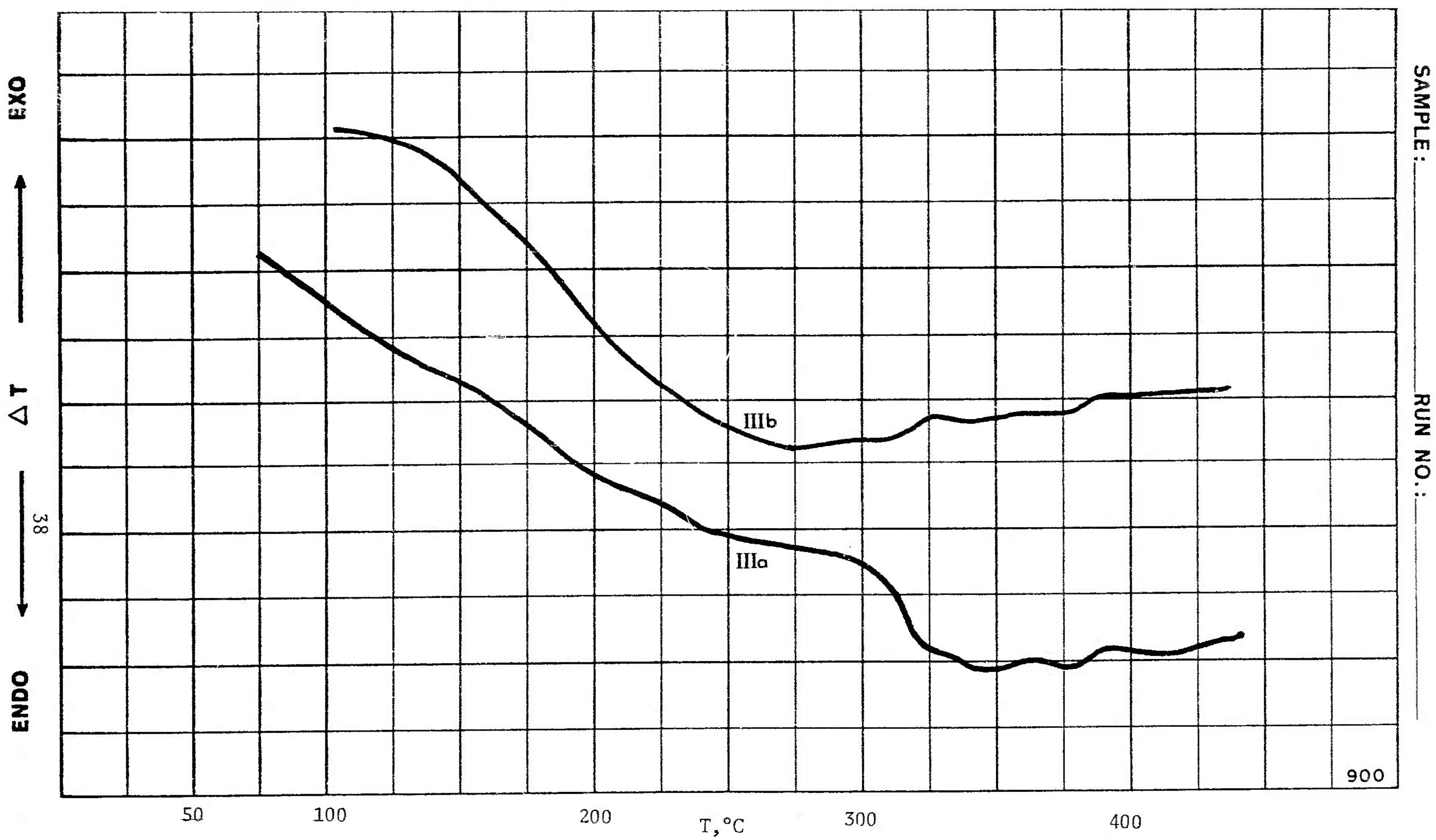


Figure 22

DSC Curves of Polymer Film IIIa and IIIb

suggesting the dimerization of 14 or an addition product of triphenylmethyl radical with 14 could be detected. In the mass spectrum, peaks corresponding to benzophenone, diphenyl and phenol could be observed. This suggests that triphenylmethyl hydroperoxide decomposes in the following manner and does not effect crosslinking due to the weak reactivity of the radicals.

$$(C_6H_5)_3COOH \longrightarrow (C_6H_5)_3CO\cdot + \cdot OH$$

$$(C_6H_5)_3CO\cdot \longrightarrow C_6H_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_5 + C_6H_5\cdot$$

$$C_6H_5\cdot + \cdot OH \longrightarrow C_6H_5OH$$

$$2C_6H_5\cdot \longrightarrow C_6H_5\text{-}C_6H_5$$

C. Carbenes as Crosslinking Additives

Carbenes react with aromatic nuclei by addition across a carbon-carbon bond or insertion into carbon-hydrogen bonds.[13] Thus, compounds which generate biscarbene intermediates would be potential crosslinking agents for aromatic polymers. Unfortunately, the generation of most carbenes requires the evolution of a volatile material or the treatment of the carbene precursor with a metal or a strong base. The latter is to be avoided in a crosslinking system, but the former could possibly be tolerated if the concentration of the crosslinking agent is low. Therefore, certain bisdiazo compounds would offer potential crosslinking agents for aromatic and aromatic heterocyclic polymers.

1. 4,4'-Bis(α-diazobenzyl)diphenyl ether (28)

4,4'-Bis(α-diazobenzyl)diphenyl ether (28) has been synthesized as a candidate for a crosslinking agent capable of generating carbenes. The synthesis of 28 has been reported as outlined in Figure 23.[14] The dihydrazone 27 has been formed in a 47% yield by the reaction of the diketone 20 with hydrazine hydrate in refluxing propanol. Oxidation of 27 with freshly activated manganese dioxide in methylene dichloride afforded diazo compound 28 in a 92% yield. Diazo compound 28 decomposes at 117-118° with vigorous evolution of nitrogen. The physical properties of 28 are shown in Table 9 and the DSC curve is shown in Figure 24.

As a model compound, α-diazodiphenylmethane 30 has been synthesized from benzophenone through benzophenone hydrazone. Benzophenone hydrazone 29 was prepared by heating benzophenone with 99% hydrazine hydrate in n-butanol: m p 97.5-98.0° (lit [15] m p 98°). The oxidation of 29 was performed under identical reaction conditions as used for the preparation of 28. α-Diazodiphenylmethane 30 was obtained as a deep purple oil and ir analysis showed a characteristic absorption of diazo group at 2040 cm^{-1}.

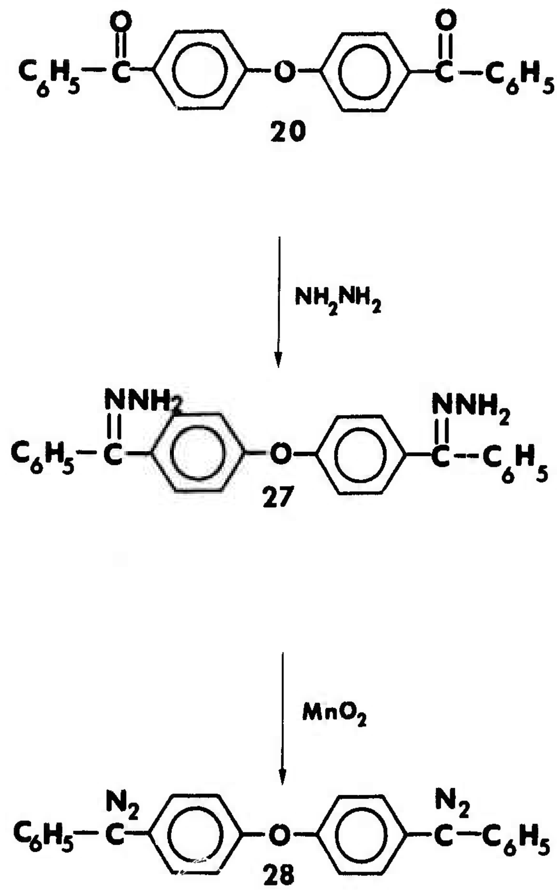


Figure 23

Synthesis of 4,4'-Bis(α-diazobenzyl)diphenyl ether (28)

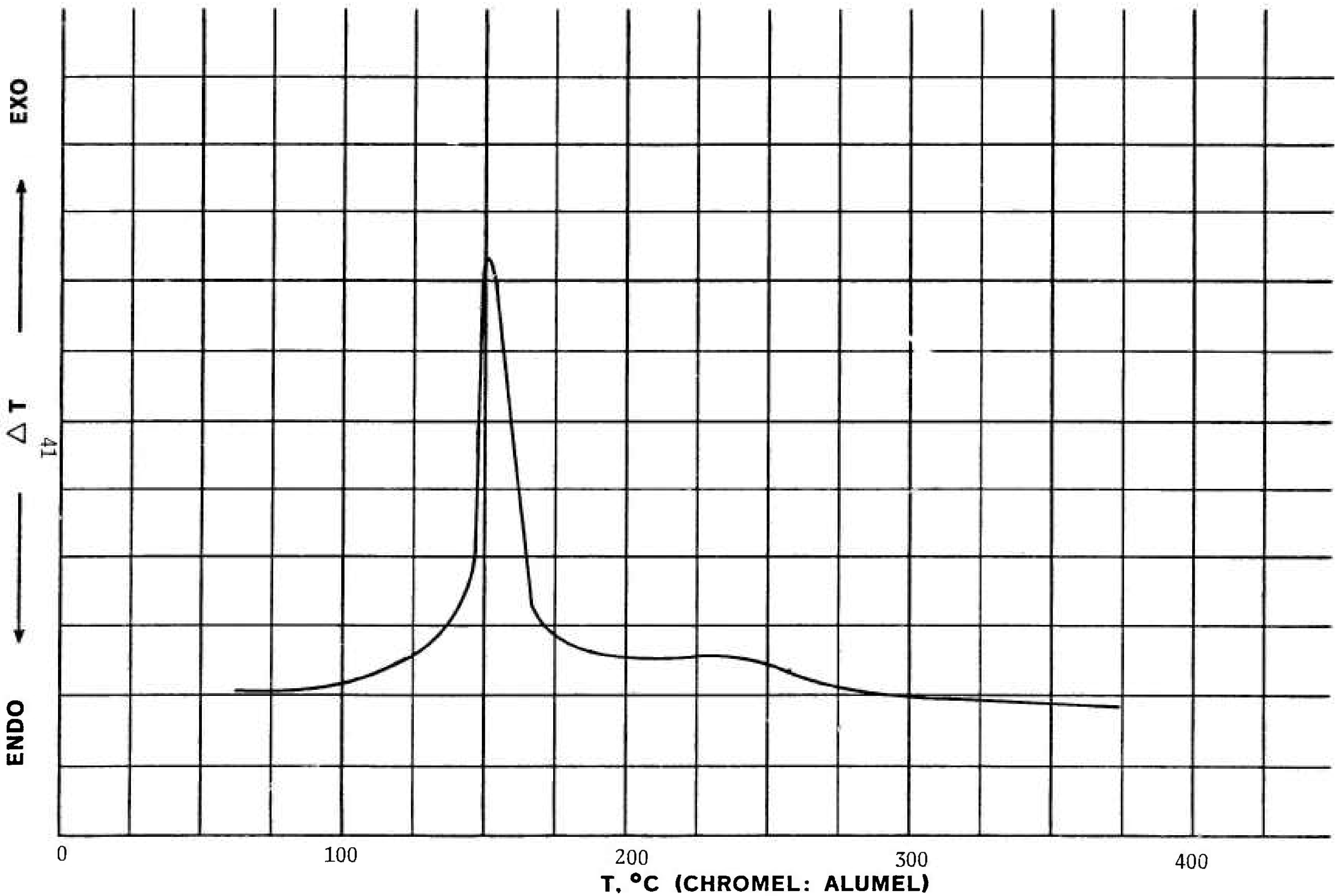


Figure 24

DSC Curve of 4.4'-Bis(α-diazobenzyl)diphenyl ether

Table 9

Physical Properties of 28

m.p.	117-118° (lit.[14] 126-28°)
Decomp. temp. by DSC (Heating rate=20°/min. in N_2)	150°
Compatibility with polymers 2, 3 and 4	yes
Solubility in $CHCl_3$	yes

2. Preparation and Curing of Films Containing 4,4'-Bis(α-diazobenzyl)diphenyl ether (28)

The effectiveness of the bisdiazo compound, 28 as a crosslinking agent for polyquinoxaline 2, polyquinolines 3 and 4, polyanthrazoline 5 and polyisoanthrazoline 6 has been investigated. The preparation and the physical properties of the polymers have been reported in earlier sections.

Polymer films of 2, 3 and 4 including 28 were cast from chloroform solutions containing 5-10% solids. Films were cast and air dried. Thermal crosslinking of these polymer films were carried out by heating the films in a mercury bath under a nitrogen atmosphere. The conditions of the heat treatment and the results are given in Table 10. The DSC traces of IIIa and IVa are shown in Figure 25.

The crosslinking agent has good compatibility with all polymers both before and after the heat treatment. Furthermore, the expected evolution of volatile material which is generated during the heat treatment did not have an undesirable influence upon the film. Undesirable bubble formation was avoided because of the low concentration of the crosslinking agent.

The ir absorption at 2050 due to the diazo group of 28 appeared in the film IVb, but disappeared completely after the heat treatment.

The comparison of the DSC traces of the heat treated film IVa with the heat treated film IIIa without the addition of any additive is given in Figure 25. No distinct transition could be observed in IVa.

All samples, both cured and uncured films, are still readily soluble in chloroform, indicating the absence of a network structure.

Table 10

Polyquinoxaline 2 and Polyquinoline 3 and 4 Films including 4,4'-Bis(α-diazobenzyl)diphenyl ether (28)

No.	Film Composition (wt/wt)	Heat Treatments[a]	Appearance	Solubility in $CHCl_3$
IIIa	2	yes	yellow transparent	soluble
IIIb	2	no	yellow transparent	soluble
IVa	2/28 (100/5)	yes	orange brown transparent	soluble
IVb	2/28 (100/5)	no	yellow transparent	soluble
Va	3	yes	pale yellow translucent	soluble
Vb	3	no	pale yellow translucent	soluble
VIa	3/28 (100/5)	yes	pale orange translucent	soluble
VIb	3/28 (100/5)	no	pale yellow translucent	soluble
VIIa	4	yes	pale yellow translucent	soluble
VIIb	4	no	pale yellow translucent	soluble
VIIIa	4/28 (100/5)	yes	pale orange translucent	soluble
VIIIb	4/28 (100/5)	no	pale yellow translucent	soluble

[a] 100/2, 125/2, 150/2 and 200/2 ($^{o}C/hr$)

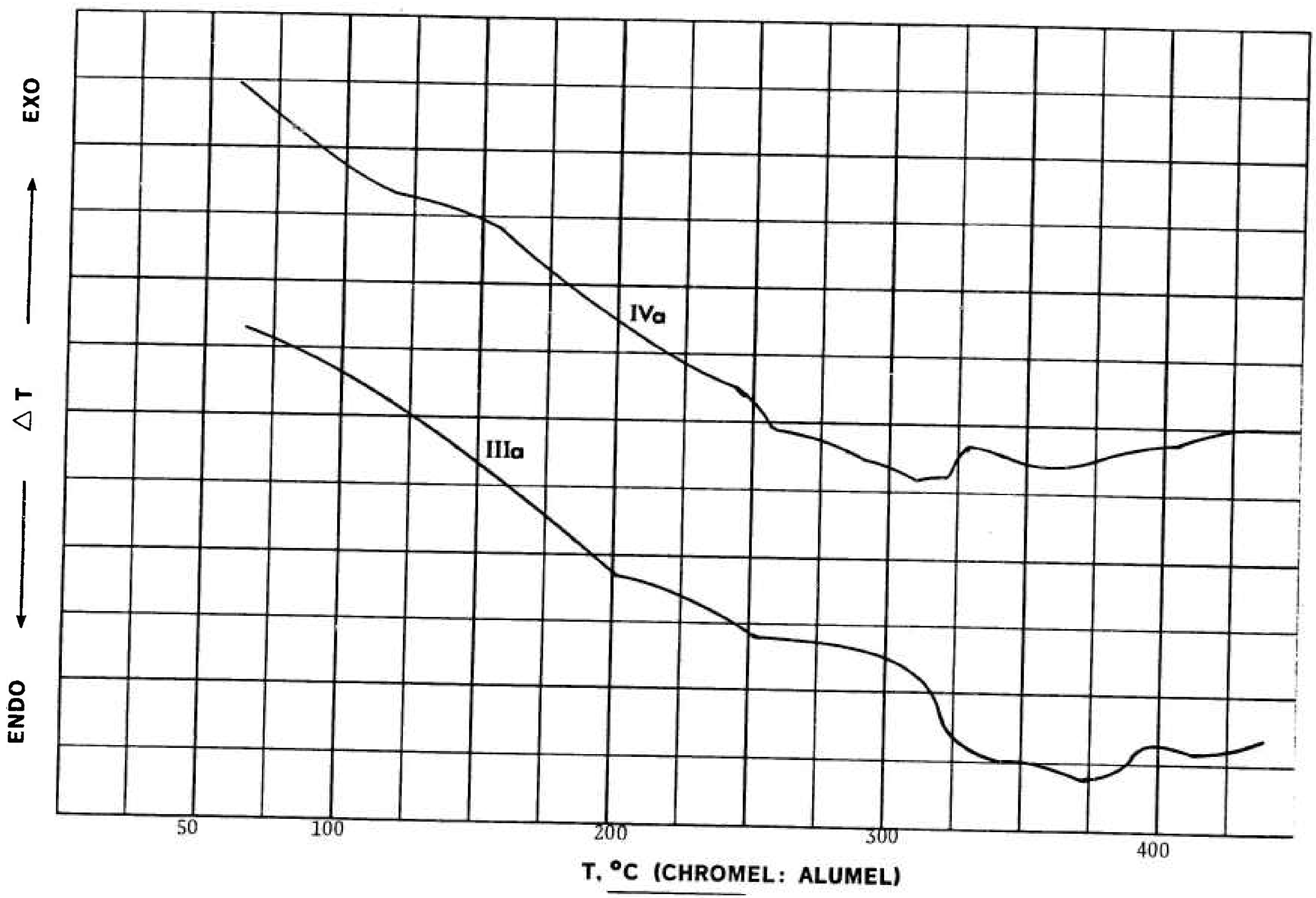


Figure 25

DSC Curve of Polymer Films IIIa and IVa

The lack of network structure was supported by the following model reaction of 2,3-diphenylquinoxaline 14 with α-diazodiphenylmethane 30. The model reaction was carried out in bulk principally at the same condition as that used for curing of polyquinoxaline 2 film containing 4,4'-bis(α-diazo-benzyl)diphenyl ether 28. Thus the mixture of equimolar amounts of 14 and 30 was heated for 2 hr each at 100°, 125°, 150°, 175° and 200°. Then, the reaction mixture was analyzed by mass spectroscopy. However, no peak suggesting the addition of the carbene to 14 could be detected.

Polyanthrazoline 5 and polyisoanthrazoline 6 are insoluble in chloroform. So, the films of these polymers including 28 were cast from trifluoroacetic acid (TFA) although TFA is not an optimum casting solvent because it reacts with 28 at room temperature to accelerate carbene formation. The films of 5 were cast also from N-methyl-2-pyrrolidone (NMP) in spite of the high boiling temperature. The results of the thermal treatment of these films is given in Table 11.

Polyisoanthrazoline film 6 could be cast from trifluoroacetic acid. However, the film including 28 could not be cast because of gellation. In the case of polyanthrazoline, the film including 28 could be cast. The film containing 28 is tougher than the film which was cast without 28.

Crosslinking takes place during film casting. The crosslinking might be due to ylide formation between the anthrazoline or isoanthrazoline and the biscarbene which has been generated from the bisdiazocompound 28. The carbene generation is accelerated by trifluoroacetic acid.

Carbenes are assumed to react with amines to produce ylides, which rapidly undergo Stevens rearrangements, for example the reaction of carbene with pyridine to give α-picoline[16] and the formation of 9-benzyl-9-dimethylaminofluorene from diazofluorene and N,N-dimethylbenzylamine.[16] However, the ylide formed by the reactions of anthrazoline or isoanthrazoline cannot be stabilized by the further Stevens rearrangement because the α-positions are blocked.

All of the cured films obtained are still readily soluble in trifluoroacetic acid.

In order to confirm the possibility of the crosslinking, the model reactions of 2,4,6,8-tetraphenyl-1,9-anthrazoline (15) or 2,4,7,9-tetraphenyl-1,6-anthrazoline (16) with α-diazodiphenylmethane (30) have been carried out. The reaction was performed in TFA. However, in both cases, the reactants 15 and 16 were recovered in higher than 80% yields and no adduct could not be isolated. These model reactions suggest that the efficiency of the crosslinking by carbenes is not high if any.

Table 11

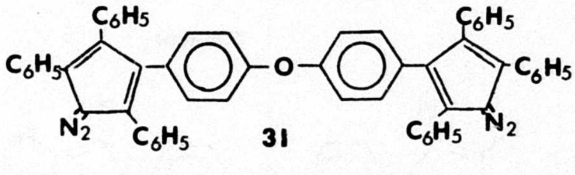
Polyanthrazoline 5 and Polyisoanthrazoline 6 including 4,4'-Bis(α-diazobenzyl)diphenyl ether (28)

No.	Additive/Polymer (wt/wt)	ηinh (H_2SO_4)	Solvent for casting	Doap	Appearance Before Cure	Appearance After Cure	Solubility in TFA Before Cure	Solubility in TFA After Cure
IX	6	0.59	TFA	clear doap	Tough	--	--	--
X	28/6 (5/100)	0.59	TFA	gellation	--	--	--	---
XI	5	0.35	NMP[a]	clear doap	Brittle	Brittle	S[c]	S
XII	28/5 (5/100)	0.35	NMP	when heated	Brittle	Brittle	S	S
XIII	5	0.35	TFA[b]	clear doap	Brittle	Brittle	S	S
XIV	28/5 (5/100)	0.35	TFA	clear doap	Tough	Brittle	S	S
XV	28/5 (5/100)	0.89	TFA	clear doap	Tough	Tough	S	S

[a]NMP: N-methylpyrrolidone
[b]TFA: Trifluoro-acetic acid
[c]S: Soluble
[d]Cure: 100°/2 hr, 125°/2hr, 150°/2hr, 175°/2hr and 200°/2hr.

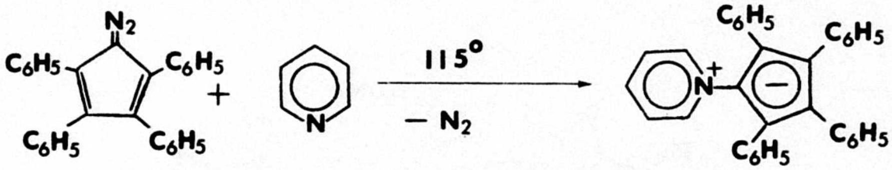
3. 2,2'-(Oxydi-p-phenylene)bis(1,3,4-triphenyldiazocyclopentadiene) (31)

In the previous section, 4,4'-bis(α-diazobenzyl)diphenyl ether has been synthesized as a candidate for a crosslinking agent capable of generating carbenes. In addition, the synthesis of 3,3'-(oxydi-p- phenylene)bis(2,4,5-triphenyldiazocyclopentadiene) (31) has been investigated.



31

Although tetraphenyldiazocyclopentadiene reacts with alkanes by insertion, it most interestingly reacts with heterocyclic aromatics such as pyridine to afford organic salts.[18]



Therefore, 31 should afford an interesting crosslinking additive, especially with the heterocyclic polymers, polyquinoxaline, polyquinoline, polyanthrazoline and polyisoanthrazoline.

a. A proposed synthetic route to the bisdiazocyclopentadiene 31 is outlined in Figure 26. The synthesis of 3,3'-(oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone) (32) has been reported.[19] The proposed synthesis of 2,2'-(oxydi-p-phenylene)bis(1,3,4-triphenyldiazocyclopentadiene) (31) is similar to the reported synthesis of tetraphenyldiazocyclopentadiene.[20] However, attempts to synthesize the tosylhydrazone 33 has afforded an unidentified product, melting at 125-146° and showing a strong carbonyl absorption at 1715 cm^{-1}

b. Another synthetic route is shown in Figure 27. The route is analogous to the reported synthesis[14] of 4,4'-bis(α-diazobenzyl)diphenyl ether involving the catalytic oxidation of the hydrazone by treatment with activated manganese dioxide. The synthesis of the hydrazone 34 was carried out by heating 32 with excess hydrazine hydrate in isopropyl alcohol for 19 hr. The product thus obtained, however, shows the carbonyl absorption at 1715 cm^{-1}.

For the investigation of the reactivity of phenylated cyclopentadienone with hydrazine, an analogous reaction was carried out by using tetraphenylcyclopentadienone. Heating the cyclopentadienone with hydrazine in isopropyl alcohol for 30 min gave white crystals melting at

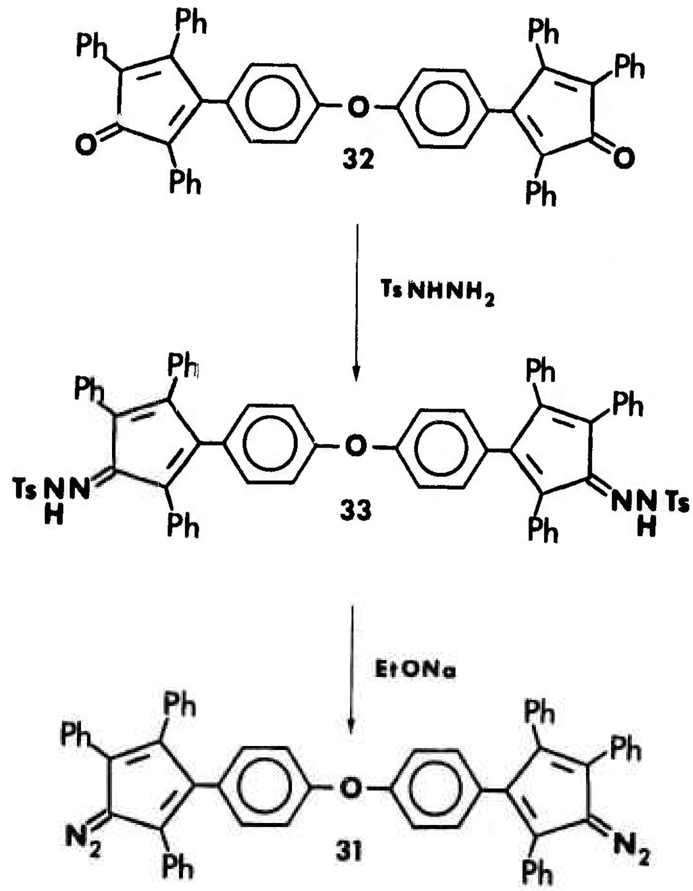


Figure 26

Proposed Synthesis of 2,2'-(Oxydi-p-phenylene)bis-(1,3,4-triphenyldiazocyclopentadiene) (31)

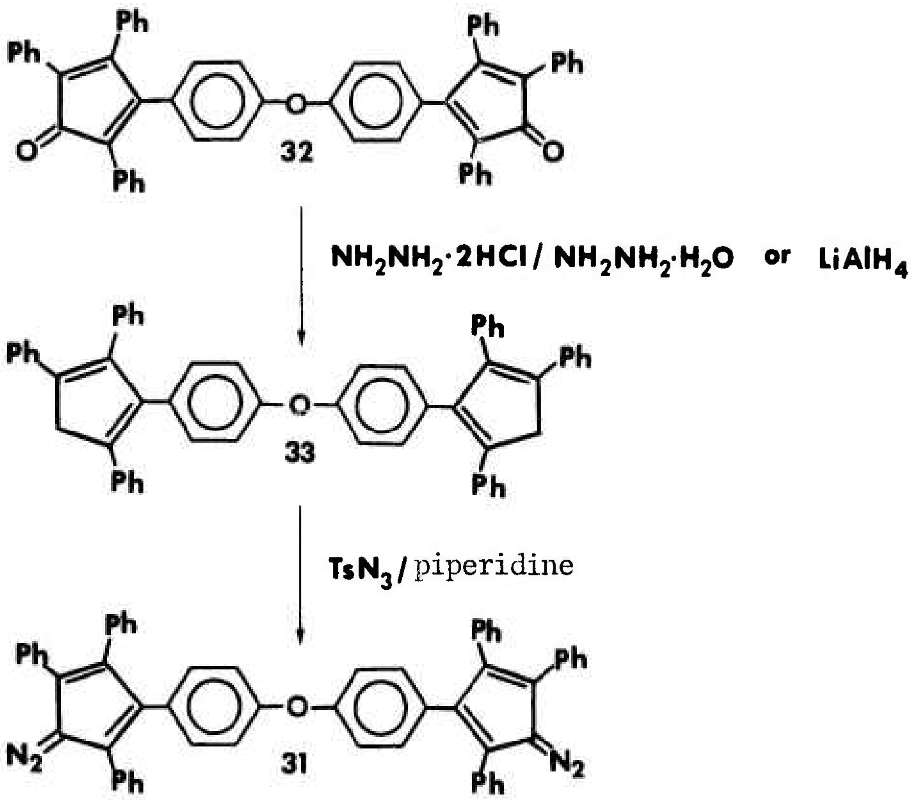


Figure 27

Proposed Synthesis of 2,2'-(Oxydi-p-phenylene)bis(1,3,4-triphenyldiazocyclopentadiene) (31)

158-159°. The ir spectrum showed a strong carbonyl absorption at 1715 cm^{-1}. On the other hand, prolonged heating for 16 hr gave orange colored crystals which melted at 137-138° (from cyclohexane). The ir spectrum showed no carbonyl absorption at 1715 cm^{-1}. The product which melted at 137-138° has been characterized to be the hydrazone of tetracyclopentadienone by using ir, nmr, mass spectrum and elemental analysis. This result is in contrast to the reported reaction of tetraphenylcyclopentadienone with hydrazine. It has been reported that hydrazine and phenylhydrazine reduce tetracyclone to dihydrotetracyclone under usual conditions.[21,22,23]

The oxidation of the hydrazone to tetraphenyl-diazocyclopentadiene, however, did not afford the diazo compound. The reaction was carried out by stirring the mixture of the hydrazone and activated manganese dioxide in methylene chloride overnight at room temperature. However, the reactant was recovered unchanged with no absorption due to diazo group observed in the infrared spectrum. Even prolonged heating at the reflux temperature gave the same result.

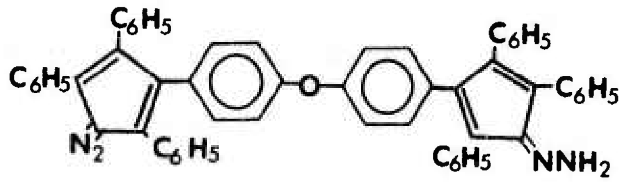
c. Another proposed synthetic route to 2,2'-(oxydi-p-phenylene)bis(1,3,4-triphenyldiazocyclopentadiene) (31) is outlined in Figure 27. The proposed synthesis of 2,2'-(oxydi-p-phenylene)bis(1,3,4-triphenylcyclopentadiene) (35) is analogous to the reported synthesis of tetraphenylcyclopentadiene.[20] One of the synthetic methods involves the reduction of 3,3'-(oxydi-p-phenylene)bis(2,4,5-triphenyldiazocyclopentadienone (32) with hydrazine; another method uses lithium aluminum hydride as the reducing agent. Heating the bistetracyclone 32 with either 85% or 99% hydrazine hydrate/hydrazine dihydrochloride, or hydrazine /hydrazine dihydrochloride in diethylene glycol gave a white powder which showed no ir carbonyl absorption near 1700 cm^{-1}. In all cases, however, thin layer chromatography (TLC) analysis showed several spots and no pure product could be obtained. Another approach to 35 was carried out by treating bistetracyclone 32 with lithium aluminum hydride/aluminum chloride in ether. The product thus obtained showed several spots in TLC and could not be fractionated by column chromatography.

Biscyclopentadiene obtained by the reduction of 32 with hydrazine was employed for the next step without any further purification (see experiments NNa-c).

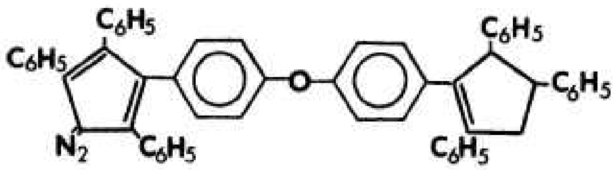
The synthesis of the bis(diazocyclopentadiene) 31 is analogous to the reported synthesis[20] of tetraphenyldiazocyclopentadiene. p-Toluene sulfonylazide was prepared from p-toluenesulfonyl chloride and sodium azide by the reported synthesis.[24] The reaction was carried out by treating 35 with p-toluenesulfonyl azide in acetonitrile at room temperature to obtain a viscous red brown oil. The viscous oil was fractionated twice by column chromatography (silica gel) eluting with benzene and benzene-ethanol (98/2) to obtain a brown powder. The ir analysis of the brown powder showed a strong absorption at 2080 cm^{-1} characteristic of the diazo group. TLC analysis showed a strong

orange spot at Rf 0.8, and some colorless weak spots at Rf 0.66, 0.55 and 0.35 (benzene/ethanol 99/1) even after the repeated purifications.

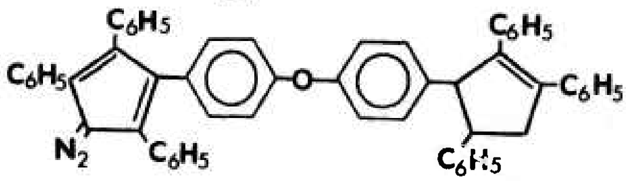
From the elemental analysis and ir analysis, the product obtained is assumed to have the following structure:



When biscyclopentadiene obtained by the prolonged reduction of 32 (experiment MM-d) with hydrazine hydrate was employed, the half diazo compound having the following structure was isolated (experiment NN-c).



OR



III. Experimental

A. 3,3',4,4'-Tetraaminodiphenyl ether (7a)

3,3',4,4'-Tetraaminodiphenyl ether (7a) was prepared according to the published procedure[25] as outlined in Figure 28. Repeated recrystallization of the tetrahydrochloride salt from 6N hydrochloric acid afforded white needles of the salt. Recrystallization of 7a was carried out in deoxygenated water containing a small amount of sodium dithionite under a nitrogen atmosphere.

B. 3,3'-Diaminobenzidine (7b)

3,3'-Diaminobenzidine (7b) was obtained commercially and was purified by recrystallization from deoxygenated water.

C. 4,4'-Oxydibenzil (8)

4,4'-Oxydibenzil (8) was obtained commercially, eluted from a silica gel column with chloroform and recrystallized from 95% ethanol.

D. Poly[2,2'-(p,p'-oxydiphenylene)-6,6'-oxybis(3-phenylquinoxaline)] (1)

To a 500 ml resin flask fitted with a nitrogen inlet/outlet and mechanical stirrer and containing 14.6522g (63.6300 mmol) of 3,3',4,4'-tetraaminodiphenyl ether (7a) and 100 ml of m-cresol and xylene (1:1) was added 27.6440g (63.6300 mmol) of 4,4'-oxydibenzil (8). An additional 160 ml of solvent (1:1, m-cresol: xylene) was added to assure complete transfer of monomers. After 2 hr, 60 ml of xylene was added and after 6 hr an additional 20 ml of xylene afforded a viscous amber mixture of 12.5% solid content. An additional 100 ml of xylene after 11 hr was added. After a total of 18 hr of reaction in a nitrogen atmosphere, the polymerization mixture was poured into 2ℓ of ethanol in a blender to give polymer 1 as an off-white fibrous material. The polymer was dissolved in chloroform, filtered, reprecipitated into methanol and dried for 12 hr at 135° under reduced presssure to afford 35.4g (94.0%) of 1. The inherent viscosity was determined in m-cresol at 25.0° and had a value of 2.8 dl/g. Physical properties for 1 are given in Table 2.

E. Poly[2,2'-(p,p'-oxydiphenylene)-6,6'-di(3-phenylquinoxaline)] (2)

A total of 10.7136g (50.0000 mmol) of 3,3'-diaminobenzidine was slowly added to a solution of 21.7227g (50.0000 mmol) of 4,4'-oxydibenzil in 150 ml of 1:1 m-cresol: xylene. The solution was then stirred at 20° for 18 hr. The resulting viscous solution was slowly added to 750 ml of vigorously stirred absolute ethanol. The resulting polymer was filtered,

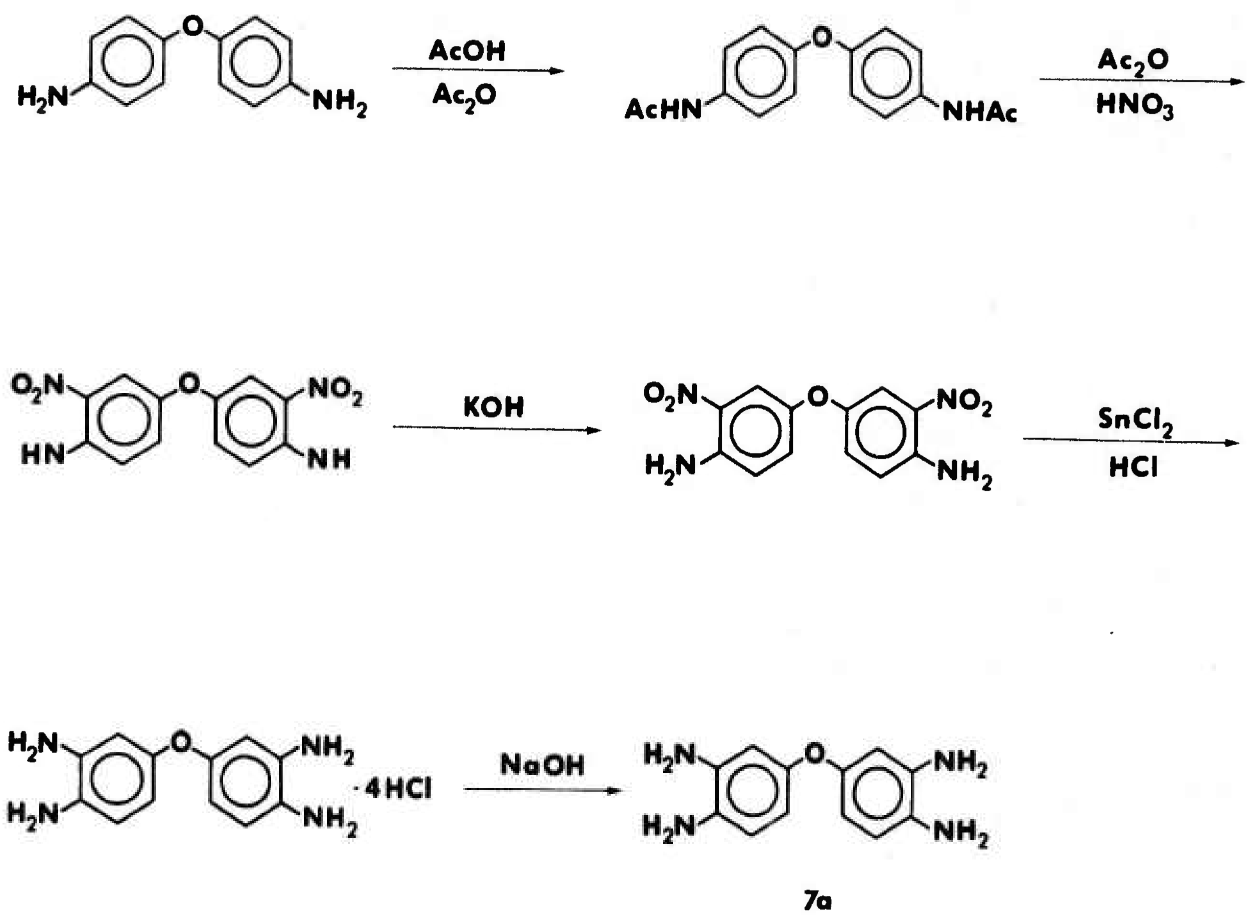


Figure 28

Synthesis of 3,3',4,4'-Tetraaminodiphenyl ether (7a)

washed with ethanol and dissolved in 1ℓ of chloroform. This solution was filtered and added to 1ℓ of stirred ethanol. The polymer was then filtered and dried under a high vacuum at 135°. The resulting polymer weighted 28.0g (97.3%) and had an inherent viscosity in m-cresol at 25.0° of 1.01 dl/g. Physical properties of 2 are given in Table 2.

F. 4,4'-Bis(2-aminobenzoyl)diphenyl ether (9)

Potassium hydroxide (26g, 450 mmol) was dissolved in 320 ml of water and cooled to 5° with an ice bath. 4,4'-Bis(2-carbamylbenzoyl)diphenyl ether (20g, 43 mmol) was added all at once and allowed to stir for 15 min. Addition of 140 ml (97 mmol) of 5.25% sodium hypochlorite solution over a 15 min period effected solution. The solution was heated on a steam bath to 80° within a 15 min period, whereupon a yellow precipitate began to form. The reaction temperature was maintained between 80 and 85° for an additional hr and then cooled and filtered to give 16.8g (95%) of 9 as a fine yellow powder. Recrystallization from 95% ethanol gave bright yellow needles: mp 136-137.5%; ir(KBr) 3460, 3350 (N-H), 1625 (C=O), 1245 cm^{-1} (C-O-C). For ^{13}C-nmr spectrum ($CDCl_3$) see Table 3.

G. Poly[2,2'-(p,p'-oxydiphenylene)-4,4'-(p,p'-oxydiphenylene) diquinoline] (3)

Method a. In a 100 ml resin flask fitted with a nitrogen inlet and mechanical stirrer was placed 3.2g of 85% phosphoric acid and the nitrogen flow begun. Phosphorus pentoxide (4.8g) was then added while the phosphoric acid was stirred and cooled in an ice bath. The mixture was heated to 140° over a 1 hr period and maintained at that temperature for an additional hr. The 84% polyphosphoric acid (PPA) was allowed to cool under nitrogen to 90°. Into a 30 ml beaker was weighed 1.6338g (4.0000 mmol) of 4,4'-bis(2-aminobenzoyl)diphenyl ether and 1.0172g (4.0000 mmol) of diacetyldiphenyl ether. The monomers were added all at one to the PPA and then 25ml of m-cresol was used to wash all traces of monomer into the reaction flask. This afforded a monomer content of 7.7%. The polymerization was heated under a static nitrogen blanket as follows: 85-95° for 8.5 hr, 95-170° for 1.5 hr, 170-175° for 4 hr, 175-190° for 0.5 hr and 190-195° for 23.5 hr.

The dark brown clear mixture was then poured into 500 ml of ethanol to give a yellow precipitate. The polymer was filtered and stirred with aqueous sodium hydroxide to give a tan powder. The polymer was then washed again with hot aqueous sodium hydroxide with hot water twice, with methanol and hot methanol twice. The polymer was dried in an oven at 80° and then at 110° in vacuo. Yield=2.362g (100%).

η_{inh}=0.18 in $CHCl_3$ at 25.0°, c=0.500g/dl
η_{inh}=0.24 in m-cresol at 25.0°, c=0.500g/dl
Very brittle film was obtained from dilute m-cresol soln.

TGA: % wt loss in N_2 at 800°=25
break in N_2=530°
break in air=500°
ir(KBr) 1600, 1495, 1240 (C-O-C), 880, 860, 846, 765 cm^{-1}

Method b. The PPA (8g) was prepared as in method a with the exception that it was heated under nitrogen at 145° for 7 hr. m-Cresol (15 ml) was then added to give a homogeneous clear solution. The PPA/m-cresol mixture was then allowed to cool to 80° and 1.6338g (4.0000 mmol) of 4,4'-bis(2-aminobenzoyl)diphenyl ether and 1.0172g (4.0000 mmol) of 4,4'-diacetyldiphenyl ether were added all at once to the solvent. An additional 10 ml of m-cresol was added to assure complete transfer of the monomers from the beaker. Solution of the monomers was complete within 5 min to give a yellow solution. The polymerization was heated as follows: 80-90° for 0.5 hr, 90-100° for 9 hr, 110-150° for 1.5 hr, 150-170° for 6 hr, 170-190° for 0.5 hr at 190-200° for 55 hr. The color of the reaction mixture remains yellow to orange below 170°, and rapidly turns brown at 190°. Solution was complete throughout the reaction. The reaction mixture was allowed to cool and was poured into 500 ml of methanol to give a yellow fibrous material, (protonated polyquinoline). The polymer was filtered and stirred in aqueous sodium hydroxide to give an off-white material. The polymer was then filtered, sucked as dry as possible and dissolved in chloroform. The brown solution was filtered into Skelly B to give a fluffy white material. The polymer was dried at 100° *in vacuo* to give 2.338g (98.8%) of an off-white powder. The protonated polymer is not soluble in chloroform.

η_{inh}=0.57 in m-cresol at 25.0°, c= 5.00g/dl
Tan translucent films can be prepared from 10% solution in chloroform or from m-cresol/chloroform (1/1) solutions.

TGA: air break=510°
DSC: doesn't show a polymer melt temperature or glass transition (inconclusive) up to 460°
ir(film) 1600, 1495, 1240 (C-O-C), 880, 860, 838, 765 cm^{-1}

H. 4,4'-Di(2-quinoxalyl)diphenyl ether (14)

A mixture of o-phenylene diamine (3.25g, 30.0 mmol) and benzil (6.30g, 30.0 mmol) in dioxane(200 ml) and water(100 ml) was heated for 5 hr under reflux. The mixture was cooled to room temperature and kept in the refrigerator overnight. The white needles precipitated were collected by filtration and washed with dioxane/water (60/30) to give 6.1g (71%) of 14: mp 125-126°; ir(KBr) 3075, 3040, 1480, 1445, 1350, 775, 765 and 705; ^1H-nmr($CDCl_3$) 1.8-2.9(m)τ; MS, m/e 282, 281, 178,153, 104 and 77 MW calcd: 282; Anal. Calcd for $C_{20}H_{14}N_2$: C,85.08; H,5.00; N,9.92. Found C, 84.95; H,4.95; N,9.91.

I. 2,4,6,8-Tetraphenylanthrazoline (15)

A mixture of 4,6-dibenzoyl-m-phenylene diamine (3.16g, 0.01 mol) and acetophenone (2.41g, 0.02 mol) in 50g of polyphosphoric acid was heated with stirring at 120° for 20 hr. During the reaction, the color of the reaction mixture turned from yellow to brownish black. The reaction mixture was poured into 300 ml of water with mechanical stirring. The orange powder precipitated was collected by filtration and washed repeatedly to obtain 4.60g of orange powder: mp254-263°. The powder was suspended in 225 ml of ethanol and the suspension was heated under reflux for 30 min. The insoluble part was collected by hot filtration to obtain 3.8g (79%) of 15: mp 263-265°; ir(KBr) 3075, 3040, 1605, 1580, 1460, 1360, 1250, 765 and 705 cm^{-1}; MS, m/e 486, 485, 484, 407, 301, 277 and 242 MW calcd: 484; Anal. Calcd. for $C_{36}H_{24}N_2$: C, 89.22; H, 4.99; N, 5.78 Found: C, 88.98; H, 5.18; N, 5.84.

J. 2,4,7,9-Tetraphenylisoanthrazoline (16)

A mixture of 2,5-dibenzoyl-p-phenylenediamine (1.58g, 5.00 mmol) and acetophenone (1.21g, 10.0 mmol) in 30g of polyphosphoric acid was heated with stirring at 120° for 20 hr. During the reaction, the color of the reaction mixture turned from yellow to brownish black. The reaction mixture was then poured into 300 ml of water with mechanical stirring. The orange powder which precipitated was collected by filtration and washed repeatedly to obtain 2.2g of a yellow powder. The powder was suspended in 200 ml of ethanol and the suspension was heated under reflux for 30 minutes. The insoluble part was collected by hot filtration to obtain 1.99g of 16: mp 375-378°; ir(KBr) 3075, 3040, 1605, 1590, 1540, 1580, 1450, 1360, 900, 770 and 700 cm^{-1}; MS, m/e 486, 485, 484, 400, 301, 277 and 242 MW calcd: 484; Anal. Calcd for $C_{36}H_{24}N_2$: C 89.22; H, 4.99; N, 5.78. Found: C, 89.07; H, 5.10; N, 5.83.

K. Mechanical Testing (See Table 4 and Figures 4-7)

DSC measurements were carried out on a Du Pont 900 Thermal Analyzer. Tensile testing and elongation measurements were carried out on Micro Dog-Bone samples of film which were cast from m-cresol and chloroform solvent. Modulus data was obtained on a Vibron instrument at 110 Hz over the reported temperature range.

L. Triphenylmethyl Chloride

Dry hydrogen chloride gas was bubble through a stirred suspension of triphenylmethyl alcohol (50g, 0.19 mol) in ether (200 ml) for 30 min. During the reaction, the mixture became clear. After partial removal of the solvent, the white crystals precipitated were collected by filtration and washed with cold ether to obtain 50.6g (95%) of triphenylmethyl chloride: mp97-98°.

M. Triphenylmethyl peroxide (17)

To a solution of 6.0g (22 mmol) of triphenylmethyl chloride in 50 ml of benzene was added 20g (0.10g-atm) of purified mercury. The mixture was then stirred and heated to the reflux temperature under a nitrogen atmosphere. After 8 hr, the solution was filtered through sintered glass and the solution was exposed to the atmosphere for 12 hr. The white precipitate which formed was filtered and washed well with acetone. Recrystallization from chloroform/Skelly C (30/70) afforded 2.3g (41%) of 17: mp 177-178° (lit[8] 184-186°); ir(KBr) 975, 776, 758 and 700 cm^{-1}; Anal. Calcd. for $C_{38}H_{30}O_2$: C, 88.00; H,5.83. Found: C, 88.03; H,5.50.

N. Preparation and Curing of a Film Sample of 2

A solution of 5.0g of 2 in 50 ml of chloroform was prepared. A total of 0.250g (5wt%) of 17 was added to the solution. The peroxide would not totally dissolve until another 60 ml of solvent was added. The resulting solution was filtered and 80 ml of solvent was removed under high vacuum. The films were cast on a glass plate with the aid of a doctor knife. As the chloroform solvent evaporated crystals of the peroxide formed affording a heterogeneous film.

The film sample was cured by placing the film flat in the bottom of an Erlenmeyer flask fitted with a ground glass joint. The flask was evacuated to a pressure of less than 0.01 torr. The flask was then immersed in an oil bath and was kept at a temperature of 225-230° for 3.5 hr. After allowing the sample to cool to room temperature, the film was removed and tested for solubility and thermal transitions.

O. Preparation and Curing of a Film Sample of 2

A total of 2.5g of 2 was dissolved in 15 ml of chloroform to afford a 15wt% solution of the polymer. To this was added 0.0162g (6.5% of solids) of 18. Films were then cast from this solution onto a glass plate with the aid of a doctor knife. The chloroform solvent was then allowed to evaporate at toom temperature affording a transparent, uniform film.

The film sample was thermally cured by placing it in an oven at 115-125° for 2 hr. After allowing the film to cool to room temperature, the transparent film was tested for solubility and thermal transitions.

P. 4,4'-Dibenzoyldiphenyl ether (20)

A total of 68g (0.40 mol) of benzoyl chloride was added dropwise to a slurry of 120g (0.90 mol) of aluminum chloride and 30g (0.28 mol) of diphenyl ether in 200 ml of carbon disulfide which was kept at a temperature of 0-5° by immersion in an ice bath. After the addition was complete, the slurry was stirred at 0° for 20 min and at room

temperature for 30 min. The solution was then poured onto 1 kg of ice which contained 150 ml of concentrated hydrochloric acid. The resulting white powder was recrystallized from ethanol to afford 53.6g (72%) of **20**: mp 164-165° (lit[9] 163-164°); ir(KBr) 1650 (C=O) and 1265 cm^{-1} (phenyl ether).

Q. 4,4'-Bis(diphenylchloromethyl)diphenyl ether (**21**)

A Grignard solution made from 25.2g (0.160 mol) of bromobenzene and 5.4g (0.22g-atm) of magnesium in 100 ml of anhydrous ether was slowly added to a slurry of 15.1g (0.0360 mol) of **20**. The solution was stirred for 4 hr at 25° and heated to maintain reflux for 1 hr. The solution was poured onto 500g of ice containing 75 ml of concentrated sulfuric acid. The ether layer was separated, dried over calcium chloride and saturated with anhydrous hydrogen chloride gas. The resulting white powder was filtered, washed with cold ether and air dried to afford 12.6g (60.0%) of **21**: mp 171-173° (lit[9] 173-175°); ir(KBr) 1240 cm^{-1} (phenyl ether) and with no carbonyl or hydroxyl absorption detected.

R. 4,4'-Bis(diphenylmethyl)diphenyl ether (**22**)

Small portions of zinc dust were slowly added to a hot solution of 12.6g (22.1 mmol) of **21** in 500 ml of glacial acetic acid until the red solution became completely colorless. The solution was then allowed to reflux for an additional 5 min and was then filtered hot. A total of 75 ml of water was added slowly, and the solution reheated to reflux and then allowed to cool. The resulting white precipitate was collected by filtration and was washed well with water and dried under reduced pressure to afford 9.2g (83%) of **22**[9].

S. Triphenylmethyl hydroperoxide (**23**)

Finely powdered triphenylmethyl chloride (20.0g, 0.067 mol) and 8 ml of 50 wt % aqueous sodium hydroxide were added in portions to a solution of acetone (160 ml) and 30% hydrogen peroxide (80 ml) with stirring over a period of 3.5 hr at 4-5°. The mixture was kept at 0° for 2 days. The sodium chloride byproduct was then removed by filtration. The filtrate was diluted with ether (300 ml), washed with water, dried over an anhydrous sodium sulfate and concentrated by distillation under reduced pressure at room temperature. Petroleum ether was added to the residual oil (200 ml) to obtain 12.8g (64.4%) of triphenylmethyl hydroperoxide as white crystals: mp82-83° (lit[12] 84-85°); ir(KBr) 3460(OH), 1600 (C=C), 1495, 1450, 765, 750 and 710 cm^{-1}.

T. 4,4'-Bis(diphenyl hydroxymethyl)diphenyl ether (**24**)

A Grignard solution prepared from 45.4g (0.360 mol) of bromobenzene and 9.8g (0.40 g-atm) of magnesium in 200 ml of dry ether was added to a slurry of 13.7g (0.730 mol) of 4,4'-dibenzoyldiphenyl ether in 200 ml of dry ether with stirring for 4 hr at room temperature, and heated under reflux for 2 hr. The mixture was poured onto 500g of ice

containing 75 ml of concentrated sulfuric acid. The ether layer was separated, washed with aqueous sodium carbonate, water and aqueous sodium chloride, and dried over anhydrous magnesium sulfate. After removal of the solvent, the residual viscous oil was recrystallized from benzene-petroleum ether to give 17.6g (91%) of 24: mp 71-74°. Two recrystallizations afforded 13.2g (68%) of 24: mp76-78°; ir(KBr) 3450, 1600, 1495, 1445, 1240, 1010, 765 and 695 cm^{-1}; TLC analysis (silica gel) showed single spots with each of the following solvents: Rf 0.10 (Benzene), 0.40 (benzene/ether, 96/4) and 0.80 (benzene/ether, 80/20).

U. Attempted Preparation of 4,4'-Oxybis(triphenylmethyl peroxide) (19)

Method a: from 22 and 23.

A mixture of 4,4'-bis(diphenylmethyl)diphenyl ether (2.01g, 4.00 mmol), triphenylmethyl hydroperoxide (5.52g, 20.0 mmol) and cuprous chloride (0.04g, 0.2 mmol) in ethyl acetate (20 ml) was heated at 65° with mechanical stirring for 22 hr. During the reaction a white powder precipitated. The precipitate (2.05g) was collected by hot filtration: mp 174-174.5° (decomp.); Ir analysis showed the powder to be triphenylmethyl peroxide.

After cooling the filtrate, additional triphenylmethyl peroxide (0.04g) was collected by filtration: mp 175-175.5°. The filtrate was concentrated under reduced pressure giving a red-brown viscous oil. The ir(neat) spectra showed bands at 1660, 1600, 1490, 1450, 1235, 1220 (shoulder), 750 and 650 cm^{-1}. No absorption characteristic of triphenylmethyl alcohol which could be a byproduct in this reaction was observed. The absorption at 1660 cm^{-1} is possibly due to the carbonyl of an aromatic ketone.

Method b: from 23 and 24

A solution of triphenylmethyl hydroperoxide (2.76g, 10.0 mmol) in benzene (5 ml) was added with stirring over a period of 10 min to a mixture of 4,4'-bis(diphenyl hydroxymethyl)diphenyl ether (24) (2.67g, 5.00 mmol), magnesium sulfate (1.0g) and perchloric acid (2 drops) in benzene (10 ml). The reaction mixture was stirred at 40° overnight to give a brown mixture. The mixture was separated into a benzene-soluble part (A) and insoluble part (B) by filtration. From A, unreacted triphenylmethyl hydroperoxide and 24 were detected by TLC and 0.48g of the mixture of triphenylmethyl alcohol and triphenylmethyl peroxide were isolated as crystals. Fraction B was washed with acetone. The acetone insoluble part was washed with water to remove magnesium sulfate and 0.17g of triphenylmethyl peroxide was isolated.

The reaction was also carried out in dioxane and similar results were obtained.

Method c: from 23 and 21

A solution of triphenylmethyl hydroperoxide (1.38g, 5.00 mmol), 4,4'-bis(diphenyl dichloromethyl)diphenyl ether (21) (1.43g, 2.50 mmol) and 1.0g (10 mmol) of triethylamine was heated at 40° for 8 hr and 60° for 18 hr. TLC (silica gel) analysis gave two main spots which correspond to triphenylmethyl hydroperoxide and 21, and only a weak spot at Rf 1.0 (benzene/ether, 96/4).

Method d: from 21 and triphenylmethyl chloride

To a solution of 4,4'-oxybis(triphenylmethyl peroxide) (21) (2.9g, 5.0 mmol) and triphenylmethyl chloride (6.0g, 20 mmol) in freshly distilled benzene was added mercury (25g, 0.13g-atm). The mixture was then stirred and heated to the reflux temperature under a nitrogen atmosphere. After 10 hr, the orange colored solution was filtered through sintered glass and air was bubbled through the solution for 2 days at room temperature. The white powder which precipitated was removed by filtration. The filtrate was concentrated under reduced pressure to obtain a pasty product. This was fractionated by column chromatography by using a silica gel/benzene system. The fractions collected are shown in the following table:

Fraction No	Benzene eluted (ml)	Product Obtained (g)	mp (°C)
1	100	0.2324	162-165
2	"	0.3854	146-151
3	"	0.2458	146-160
4	"	0.0800	144-165
5	"	trace	164-176
6	"	trace	

The first four fractions showed nearly the same ir spectrum ir(KBr): 1610, 1500, 1455, 1250, 755 and 705 cm^{-1}. Fractions 2 and 3 were combined and further purified by chromatography (silica gel/benzene) to obtain a white powder: mp 167-168°; nmr ($CDCl_3$) 2.86 and 2.96 τ. TLC analysis (silica gel) showed several spots at Rf 7.5, 6.5, 5.5 and 3.5 (benzene/Skelly B, 40/60). The elemental analysis, C (%) 92.77 and H (%) 5.93, indicates that the compound is not the expected product 19.

V. 4,4'-Oxybis(triphenylmethyl hydroperoxide) (25)

Finely powdered 4,4'-bis(diphenyl chloromethyl) diphenyl ether (21) (5.71g, 0.010 mol) and 2.4 ml of 50 wt % aqueous sodium hydroxide were added simultaneously in portions to a solution of acetone (100 ml) and 30% hydrogen peroxide (24 ml) with stirring over a period of 2.5 hr at 1-2°. The mixture was stirred at that temperature for 2 hr and kept at 0° overnight. The sodium chloride by-product was removed by filtration. The filtrate was diluted with ether, washed with water and saturated aqueous sodium salt, dried over anhydrous sodium sulfate, and concentrated by distillation under reduced pressure at room temperature. Benzene and petroleum ether were added to the residual oil and the solution was kept in a refrigerator for 2 days to obtain 3.0g (53%) of 25 as white crystals: mp 129-130° (decomp.); ir(KBr) 3450, 1600, 1500, 1245, 760 and 700 cm^{-1}. TLC analysis (silica gel) showed single spots with each of the following solvents: Rf 0.15(benzene) and 0.55(benzene/ether,96/4). <u>Anal</u>. Calcd for $C_{38}H_{30}O_5$: C, 80.55; H, 5.34. Found: C, 80.81; H, 5.57.

W. Model Reaction between 2,3-Diphenylquinoxaline (14) and Triphenylmethyl hydroperoxide (23)

A mixture of 2,3-diphenylquinoxaline (14) (0.564g, 2.00 mmol) and triphenylmethyl hydroperoxide (23) was heated for 2 hr each at 100°, 125°, 150°, 175° and 200° under a nitrogen atmosphere. The resulting solid was analyzed by mass spectroscopy.

X. 4,4'-Dibenzoyldiphenyl ether dihydrazone (27)

The dihydrazone was prepared by refluxing 4,4'-dibenzoyldiphenyl ether (20) (31g, 82 mmol) with 58 ml (1.16 mol) of 80% hydrazine hydrate in 230 ml of freshly distilled n-propanol for 18 hr. The solution was kept overnight at room temperature. The resultant white precipitate was filtered to obtain 15.5g (47%) of 27: mp 151-161°. Recrystallization twice from n-propanol gave the purified product: mp 159-164° (lit[14] 171-174°); ir(KBr) 1235 cm^{-1} (phenyl ether) with no carbonyl absorption detected; TLC analysis (silica gel) showed a strong spot at Rf 0.40 (benzene/acetone, 95/5) and a very weak spot at Rf 0.67. The weak spot remained even after repeated recrystallization.

Y. Active Manganese Dioxide

A solution of manganese sulphate (monohydrate; 34g, 0.20 mol) in 71 ml of water and a solution of sodium hydroxide (40%; 47 ml) were added simultaneously during 30 min to a hot stirred solution of potassium permanganate (38.4g) in 240 ml of water. Manganese dioxide precipitated soon after the start as a fine brown solid. Stirring was continued for 1 hr. The solid was collected by centrifugation and washed with water until the washings were colorless. The solid was dried at 100-120° for 1 day and ground to a fine powder (26.9g) before use.

Z. 4,4'-Bis(α-diazobenzyl) diphenyl ether (28)

4,4'-Dibenzoyldiphenyl ether dihydrazone (27) (6.0g, 14 mmol) dissolved in 1.2ℓ of methylene chloride, was mixed for 1 hr with activated manganese dioxide (18g). Then, the mixture was filtered and the filtrate was concentrated under reduced pressure to give 5.5g (92%) of crude 4,4'-bis(α-diazobenzyl)diphenyl ether (28): mp 117-118° (decomp.). Recrystallization from cyclohexane gave crystalline flakes: mp 117-118° (decomp., lit[14] 126-128°); ir(KBr) 2050 (CN_2) and 1250 cm^{-1} (ether). The DSC analysis showed a strong exothermic peak at approximately 150°.

AA. Benzophenone hydrazone (29)

A mixture of benzophenone (30g, 0.16 mol) and 99% hydrazine hydrate (50g, 1.0 mol) in 230 ml of butanol was heated under reflux for 16 hr. The solvent and excess hydrazine hydrate were removed and the volume reduced to one third the original volume. This residue was kept in a refrigerator. The crystals which precipitated were collected by filtration and washed with ethanol to obtain 20g (62%) of benzophenone hydrazone (29): mp 97.5-98.0° (lit[15] mp 98°); ir(KBr) 3420, 3270, 1590, 1490, 1440, 1230, 780, 765, 705 and 695 cm^{-1}; nmr (TMS, $CDCl_3$) 2.40-2.95 (10 H, m, aromatic protons) and 4.62 τ (2H, s, NH_2 protons).

BB. α-Diazodiphenylmethane (30)

A mixture of benzophenone hydrazone (29) (3.0g, 15.5 mmol) and freshly activated manganese oxide (7.0g) in 250 ml of methylene chloride were mechanically stirred for 1 hr at room temperature. After removal of manganese oxide by filtration, the solvent was removed by distillation to dryness to obtain α-diazodiphenylmethane 30 as a deep purple oil. The product crystallized when kept in a refrigerator; ir (neat) 2040(diazo) 1600, 1500, 760 and 695 cm^{-1}. Absorptions due to NH stretching vibration of hydrazone were not observed at 3420 and 3270 cm^{-1}.

CC. The Reaction between 2,4,6,8-Tetraphenyl-1,9-anthrazoline (15) and α-Diazodiphenylmethane (30)

α-Diazodiphenylmethane (30) (0.400g, 2.00 mmol) was added to a solution of 2,4,6,8-tetraphenyl-1,9-anthrazoline (15) (0.484g, 1.00 mmol) in 3 ml of trifluoroacetic acid. The reaction mixture was allowed to stand overnight at room temperature. After removal of the solvent, the residue was fractionated and 0.386g (80.0%) of 15 was recovered.

DD. The Reaction between 2,4,7,9-Tetraphenyl-1,6-anthrazoline (16) and α-Diazodiphenylmethane (30)

α-Diazodiphenylmethane (30) (0.400g, 2.00 mmol) was added to a solution of 2,4,7,9-tetraphenyl-1,6-anthrazoline (16) (0.484g, 1.00 mmol) in 3 ml of trifluoroacetic acid. The reaction mixture was allowed to stand overnight at room temperature. After removal of the solvent, the residue was fractionated and 0.40g (83%) of 16 was recovered.

EE. The Reaction between 2,3-Diphenylquinoxaline (14) and α-Diazodiphenylmethane (30)

2,3-Diphenylquinoxaline (14) (0.564g, 2.00 mmol) and α-diazodiphenylmethane (30) (0.388g, 2.00 mmol) were dissolved in 3 ml of chloroform in order to mix the two reactants. Then the solvent was removed under reduced pressure and the residue was heated under a nitrogen atmosphere for 2 hr each at 100, 125, 150, 175 and 200°. The reaction product was analyzed by mass spectroscopy.

FF. Attempted Preparation of 3,3'-(Oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone)bis(tosylhydrazone) (33)

The biscyclopentadienone 32 was prepared from benzyl ketone and 4,4'-oxydibenzyl according to the published procedure[19]: mp 264-266°(lit[19] 256-258°). Tosylhydradrazine was prepared from hydrazine hydrate and tosyl chloride according to the published procedure: mp 106-109° (from 50/50 methanol-water) (lit 104-107°).

Method a. In a 500 ml flask fitted with a mechanical stirrer, dropping funnel, nitrogen inlet and reflux condenser was placed 3.72g (20.0 mmol) of tosylhydrazine, 7 ml of concentrated sulfuric acid and 50 ml of purified dioxane. The solution was then heated to the reflux temperature. Deoxygenated nitrogen was passed through the apparatus while a solution of 7.83g (10.0 mmol) of 3,3'-(oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone) in 300 ml of dioxane was added so as to maintain the reflux. One hr was required for the addition and then reflux was maintained for an additional 4 hr. The purple reaction mixture was cooled and then poured into 3ℓ of water, filtered and washed with water to afford a light purple powder. Ir analysis showed the powder to be starting material. Similar reactions using a 10% excess and a two-fold excess of tosylhydrazine resulted in product with appreciable ir absorption at 1715 cm^{-1}.

Method b. By a method similar to that in Method a, 1.96g (2.50 mmol) of the bistetracyclone was added to 9.30g (25.0 mmol) of tosylhydrazine. After the same reaction time as in Method a, the mixture was poured into 700 ml of water to give a tan powder: mp 138-155° dec.; ir (KBr) 1715 (weak, C=O), 1325, 1242 and 1165 cm^{-1}.

GG. Attempted Preparation of Tetraphenylcyclopentadienone tosylhydrazone (36)

Toluene-p-sulfonylhydrazine (2.10g, 11.3 mmol) and concentrated sulfuric acid (4 ml) were dissolved in purified dioxane (26 ml) and the mixture was heated to the reflux temperature. A stream of nitrogen was passed through the apparatus while a solution of tetraphenylcyclopentadienone (4.40g, 12.6 mmol) in dioxane (75 ml) was added during a 1.5 hr period. The solution was heated at the reflux temperature for an additional 2 hr and then cooled and poured into water. The precipitate was filtered and washed with water to obtain a purple powder: mp 77-172°. Ir analysis showed the strong absorption at 1715 cm-1 characteristic of the carbonyl group of cyclopentadienone.

HH. Attempted Preparation of 3,3'-(Oxydi-p-phenylene)bis (2,4,5-triphenylcyclopentadienone)bishydrazone (34)

A mixture of 3,3'-(oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone) (32) (1.56g, 2.00 mmol) and 85% hydrazine hydrate (2g) in isopropyl alcohol (20 ml) was heated at the reflux temperature with stirring for 19 hr. During the reaction, the deep purple color turned to pale orange. After the mixture was cooled to room temperature, an orange powder precipitated and was collected by filtration to yield 0.82g: mp 126-142°; Ir analysis showed the absorption at 1710 cm^{-1} due to the carbonyl group. However, the spectrum was different from that of 32.

II. The Reaction of Tetraphenylcyclopentadienone with Hydrazine Hydrate

Method a. A mixture of tetraphenylcyclopentadienone (3.84g, 10.0 mmol) and hydrazine hydrate (85% aqueous solution, 2 ml) in isopropyl alcohol (20ml) was heated under reflux for 30 min. The product was collected by filtration and washed with isopropyl alcohol repeatedly to obtain 3.37g of white powder: mp 158-159°, dec; ir (KBr) 1715, 1500, 1460, 1150, 750 and 705 cm^{-1}; Rf (silica gel) 0.20 and 0.40 (very weak) (benzene/ethanol, 98/2), and 0.85 and 0.90 (very weak) (benzene/ethanol, 80/20); ^1H-nmr ($CDCl_3$) 2.4-3.3 (20H, m), 4.9(1H, s) and 6.8 τ(3H, s, broad); MS, m/e 386, 384, 356, and 178, MW calcd: 416.53; Anal. Calcd for $C_{29}H_{24}N_2O$: C, 83.62; H,5.81; N,6.73. Found: C, 83.57; H, 5.75; N, 6.76.

Method b. A mixture of tetraphenylcyclopentadienone (3.84g, 10.0 mmol) and hydrazine hydrate (85% aqueous solution, 2 ml) was heated under reflux for 16 hr. During the reaction, the precipitate disappeared and the deep purple color changed to orange. After the solution cooled to room temperature, it was poured into water. The precipitate was collected by filtration and recrystallized from cyclohexane giving 1.2g of orange crystals: mp 137-138°; ir (KBr) 2940, 2870, 1615, 1505, 1410, 775 and 710 cm^{-1}; ^1H-nmr ($CDCl_3$) 2.5-3.4 τ(20 H,m), 5.75 τ(2H, s); MS, m/e 398, 397, 396, MW calcd: 398.51; Anal. Calcd. for $C_{29}H_{22}N_2$: C, 87.41; H, 5.56; N, 7.03. Found: C, 87.29; H, 5.73; N, 7.13. The ir analysis shows the absence of carbonyl group. The elemental analysis suggests that the compound can be identified as the hydrazone of tetraphenylcyclopentadienone. The nmr analysis supports the above assignment. The ratio of the peak area due to aromatic protons to that at 5.75 τ was 10/1. The peak at 5.75 τ for the $=NNH_2$ protons of the hydrazone of tetracyclone has been reported. Furthermore, in the mass spectrum a peak at m/e 398 which corresponds to the parent molecular ion of the hydrazone has been reported. These observations are closely related to our observations in the mass analysis. The strong peak at m/e 397 and 396 would be fragment peaks of the hydrazone. The possibility of the hydrazone of tetraphenyl cyclopentenone was ruled out by the absence of corresponding aliphatic proton peaks in nmr and that of the parent

peak at m/e 400 in the mass spectrum.

JJ. Attempted Preparation of Diazotetraphenylcyclopentadiene

The mixture of the hydrazone of tetracyclone (0.10g, 0.25 mmol) and activated manganese dioxide (0.5g) in methylene chloride (20 ml) was stirred vigorously for 16 hr at room temperature. The manganese dioxide was removed by filtration and the filtrate was concentrated to obtain a pale yellow oil. The ir spectrum was the same as that of the starting material and no absorption due to the presence of diazo group was observed.

Heating at the reflux temperature for 23 hr gave the same result and the starting material was recovered.

KK. p-Toluenesulfonyl azide

A mixture of p-toluenesulfonyl chloride (57g, 0.30 mol) and sodium azide (23g, 0.36 mol) in 90% aqueous ethanol (300 ml) was stirred for 3 hr at room temperature. The ether layer was washed three times with water and then with saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate and concentrated under reduced pressure to obtain 54g (92%) of p-toluenesulfonyl azide as a viscous oil. The product crystallized when kept in a refrigerator. The ir analysis (neat) showed the characteristic absorption due to azide group at 2130 cm^{-1}.

LL. Hydrazine Dihydrochloride

Concentrated hydrochloric acid (270 ml, 3.2 mol) was added dropwise to hydrazine hydrate (85%, 70 ml, 1.2 mol) with stirring over a period of 3 hr while cooling with an ice bath. The crystals were collected by filtration and washed with a small amount of water and then with ethanol to obtain 89g (72%) of hydrazine dihydrochloride.

MM. Attempted Preparation of 2,2'-(Oxydi-p-phenylene)bis-(1,3,4-triphenylcyclopentadiene)

Method a. A mixture of 3,3'-(oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone) (32), 85% hydrazine hydrate and hydrazine dihydrochloride in freshly distilled diethylene glycol (60 ml) was heated at 135-140° for 4 hr. During the reaction, 32 dissolved in the solvent and the color of the reaction mixture changed to pale orange. On cooling the mixture, the powder which precipitated was collected by filtration to obtain 0.29g of white powder, mp 108-130°.

The ir spectrum showed strong absorptions at 1610, 1505, 1380, 1250, 765 and 705 cm^{-1}. An absorption at 1710 cm^{-1} due to the carbonyl group of the starting material was not observed. From the filtrate, 0.29g of white powder was recovered by reprecipitation into water. The powder showed the same ir spectrum as the first crop.

TLC analysis (silica gel) showed several spots at Rf 9.5, 8.5 and 7.5 (benzene/methanol, 90/10), and at Rf 10.0, 7.5, 7.0, 6.0 and 4.0 (benzene/methanol). The two powders were combined and fractionated by column chromatography using a silica gel/benzene system. However, sharp fractionation could not be obtained. Therefore, the crude product was used for the next step (NN-a) without purification.

Method b. A mixture of 3,3'-(oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone) (32), 99% hydrazine hydrate (48 ml) and hydrazine dihydrochloride (8.4g, 78 mmol) in freshly distilled diethylene glycol (340 ml) was heated at 130-150° for 4 hr. During the reaction, the biscyclopentadienone was dissolved in the solvent and the color of the reaction mixture changed to pale orange. On cooling the mixture, a white powder precipitated and was collected by filtration to obtain 2.5g of white powder: mp 97-122°.

The ir spectrum showed strong absorptions at 1610, 1505, 1380, 1250, 765 and 705 cm^{-1}. An absorption at 1710 cm^{-1} due to the carbonyl group of the starting material was not observed. From the filtrate, 1.9g of white powder was recovered by reprecipitation into water. The powder showed the same ir spectrum as the first crop.

TLC analysis (silica gel) of the products obtained here showed several spots at Rf 8.0, 6.6, 5.8 and 3.6 (benzene/ethanol, 99/1). The crude product was used for the next step (NN-b) without purification.

Method c. Reduction of 3,3'-(Oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone) with 99% hydrazine and hydrazine dihydrochloride:

A mixture of 3,3'-(oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone) (2.4g, 3.0 mmol), 99% hydrazine (16g, 0.5 mol) and hydrazine dihydrochloride (4.2g, 0.040 mol) in freshly distilled diethylene glycol (150 ml) was heated at 135-140° for 7 hr. During the reaction, the biscyclopentadienone was dissolved in the solvent and the color of the reaction mixture changed to pale yellow. On cooling the mixture, a white powder precipitated and was collected by filtration to obtain 0.94g: mp 93-118°. The product showed an ir spectrum that was very similar to the ir spectrum for the product obtained in experiment b; TLC (silica gel, benzene/ethanol) 9.0, 6.7, 6.1, 4.9 and 3.0 (strongest); ^1H-nmr ($CDCl_3$) 2.5-3.5 (m, aromatic protons), 3.75 (s, hydrazone-NH_2), 5.85 (s, C=C-CH_2-C=C), 6.04 (s) and 6.37 (m)τ. The ratio of the peak areas was 38:2.9:0.71:0.47:2.9.

From the filtrate, 0.58g of white powder was recovered by reprecipitation into water. The powder showed the same ir spectrum as the first crop; TLC (silica gel, benzene/ethanol) 6.7, 4.9, 3.0 (main spot) and 2.0; ^1H-nmr ($CDCl_3$) 2.5-3.5 (m, aromatic protons), 5.75 (s, hydrazone-NH_2), 6.37 (m)τ. The ratio of the peak areas was 38:3.5:1.9; Anal. Calcd. for $C_{58}H_{42}N_4O$: C, 85.89; H, 5.22; N, 6.91. Found: C, 84.63; H, 5.21; N, 7.54. From this data, the main product of the reduction is probably the hydrazone of 32.

Method d. Reduction of 3,3'-(oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone) with 99% hydrazine hydrate and hydrazine dihydrochloride:

A mixture of 3,3'-(oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone) (19.2g, 0.0246 mol), 99% hydrazine hydrate (192g) and hydrazine dihydrochloride (32.8g 0.156 mol) in freshly distilled diethylene glycol (1.45ℓ) was heated at 135-140° for 100 hr. On cooling the mixture, a white powder precipitated and was collected by filtration to obtain 12.7g of white powder: mp 95-115°. It showed almost the same ir spectrum as the product obtained in experiment c; TLC (silica gel, benzene/ethanol,99/1) 0.95 (strongest), 0.7 (strong), 0.5 and 0.25; ^{1}H-nmr ($CDCl_3$) 2.5-3.5 (m, aromatic protons), 2.8(s, hydrazone-NH_2), 5.85(s,C=C-CH_2-C=C) and 6.37 (m)τ. The ratio of the peak areas was 38:2.8:0.44:0.44:2.2. Probably, the conversion to 3,3'-(oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadiene) is very low. The product was used for the next step (NN-c) without further purification.

The powder recovered from filtrate: ^{1}H-nmr ($CDCl_3$) 2.5-3.5 (m, aromatic protons), 2.8 (s, hydrazone-NH_2) and 6.37 (m) τ. The ratio of the peak areas was 38:3.8:0.62.

Method e. Reduction of 3,3'-(oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone) with lithium aluminum hydride (0.80g, 2.0 mmol) and aluminum chloride (1.25g, 9.40 mmol). The reaction mixture was stirred for 3.5 hr at room temperature and then heated under reflux for 1 hr. The excess hydride was decomposed by the addition of dilute hydrochloric acid. The mixture was filtered and the filtrate was dried over magnesium sulfate and concentrated to obtain an amorphous solid. The ir analysis showed absorptions at 1750, 1710, 1600, 1500, 1240, 760 and 700 cm^{-1}. TLC analysis (silica gel) showed several spots at 9.0, 6.5, 5.5, 4.3, 2.5, and 1.8 (benzene/ethanol, 99/1) but showed no spot at 7.5 corresponding to that of the starting material. Fractionation by column chromatography did not give purified product.

NN. Attempted Preparation of 2,2'-(Oxydi-p-phenylene)bis(1,3,4-triphenyldiazocyclopentadiene)

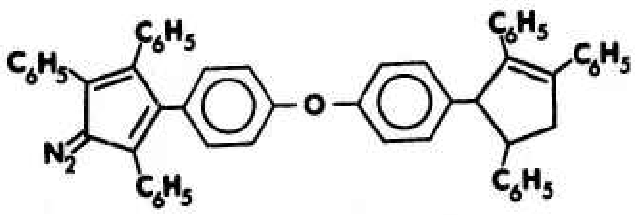
Method a. 2,2'-(Oxydi-p-phenylene)bis(1,3,4-triphenylcyclopentadiene) (2.67g, 3.55 mmol) obtained from Expt MM-a, p-toluenesulfonyl azide (1.76g, 8.90 mmol) and piperidine (2.04g, 24.0 mmol) in acetonitrile (20 ml) was stirred for 3 hr at room temperature. After removal of the solvent, the viscous oil obtained was fractionated by column chromatography by using a silica gel/benzene system. Fraction Nos. 13-19 were collected. Each of the fractions showed a strong ir absorption at 2080 cm^{-1} due to the diazo group. Furthermore, the ir spectrum showed strong absorptions at 1610 (C=C) 1510, 1245 and 705 cm^{-1}. As the fraction number increases, the relative intensity of the diazo absorption to the absorption at 1610 cm^{-1}

decreases. Each of the fractions showed three main spots at Rf 0.60, 0.40 and 0.18 in TLC (benzene/ethanol, 99.5/0.5). As the fraction number decreases, the ratio of intensities of the spots at Rf 0.60 to Rf 0.40 increases. The fractions, No. 13-19 were combined and fractionated again by column chromatography. Fraction Nos. 4-8 which correspond to the spot Rf 0.60 were combined, concentrated and triturated with Skelly B to obtain 0.085g of a brown powder: mp 122-135° (decomp.); TLC analysis showed a strong orange spot at Rf 0.80 and weak spots at Rf 0.66, 0.55 and 0.35 (benzene/ethanol, 99/1); ir(KBr) 2080, 1610, 1510, 1245 and 705 cm^{-1}; Anal. Calcd. for $C_{58}H_{38}N_4O$: C, 86.33; H, 4.75; N,6.94. Found C, 86.61; H, 5.65; N,4.40.

Method b. The product of Expt MM-b was used as the reactant. 2,2'-(Oxydi-p-phenylene)bis(1,3,4-triphenylcyclopentadiene) (4.42g, 5.85 mmol), p-toluene sulfonyl azide (2.54g, 12.9 mmol) and piperidine (3.0g, 35 mmol) in 60 ml of acetonitrile were stirred for 3 hr at room temperature. After removal of the solvent, the residual oil was fractionated twice by column chromatography (silica gel - benzene/ethanol, 98/2) in a manner described in the experiment NN-a to obtain 0.13g of a brown powder: mp 113-122° (decomp); ir spectrum identical to the powder obtained in the experiment MM-a; TLC analysis showed a strong orange spot at Rf 0.8 and two weak spots at 0.68 and 0.53 (benzene/ethanol, 99/1); Anal. Calcd for $C_{58}H_{38}N_4O$: C, 86.33; H,4.75; N, 6.94. Found: C, 84.70; H, 5.65; N, 4.25.

Method c. The product of the experiment MM-d was used as the reactant, 2,2'-(Oxydi-p-phenylene)bis(1,3,4-triphenylcyclopentadiene). A mixture of 2,2'-(oxydi-p-phenylene)bis(1,3,4-triphenylcyclopentadiene) (12.8g, 17.0 mmol), p-toluenesulfonyl azide (7.4g,38 mmol) and piperidine (8.8g, 0.103 mol) in acetonitrile (175 ml) was stirred at room temperature for 13 hr. After removal of the solvent, the viscous oil obtained was fractionated by column chromatography (silica gel - benzene/methanol, 99/1). Fractions which had an orange color were collected and a viscous oil was obtained. The oil was fractionated again by column chromatography (silica gel - benzene/methanol, 98/2). Fractions 24-28 and fractions 2-6 were collected. The former showed two yellow spots in TLC (silica gel - benzene/ethanol, 99.5/0.5) at Rf 0.75 and 0.55. The latter showed one yellow spot in TLC (silica gel) at Rf 0.95 (benzene/ethanol, 99.5/0.5) and 0.85 (Skelly B/benzene, 50/50). The former product corresponds to the product obtained in the experiment NNa and b. The latter was collected to obtain 3.7g of red brown viscous oil. Ir analysis (neat) showed strong peak at 2080 cm^{-1} due to diazo group. Furthermore, it showed two peaks at 2860 and 2950 cm^{-1} due to N-(p-toluene sulfonylamino)piperazine. The viscous oil was triturated with ethanol to remove the by-product. The brown powder weighing 0.74g was collected by fractionation, Rf (Skelly B/benzene, 50/50) 0.85 (strong yellow) 0.18 (weak yellow) and 0.00. The powder was refractionated by column chromatography (alumina-benzene) to obtain 0.14g of brown powder; mp 175-177°; Rf 0.75 (Skelly B/benzene, 50/50); ir(KBr) 2920, 2840, 2080, 1600, 1500, 1240 and 700 cm^{-1}; ^1H-nmr ($CDCl_3$) 2.65-3.60

(m, aromatic protons), 5.75, 6.35 and 8.25τ; Anal. Calcd for $C_{58}H_{40}N_2O$: C, 89.20; H, 5.16; N, 3.59. Found: C, 89.00; H, 5.39; N, 3.95. From the data, the product separated is characterized to be the following structure:



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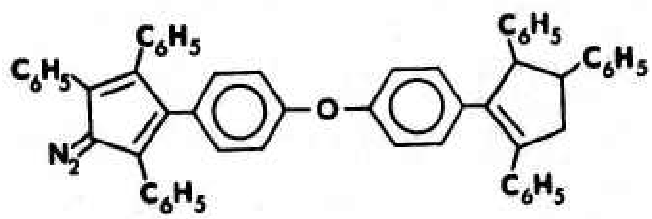

Appendix

Identification of Compounds According to Numerical Assignment

1. Poly[2,2'-(p,p'-oxydiphenylene)-6,6'-oxybis(3-phenylquinoxaline)]
2. Poly[2,2'-(p,p'-oxydiphenylene)-6,6'-di(3-phenylquinoxaline)]
3. Poly[2,2'-(p,p'-oxydiphenylene)-4,4'-(p,p'-oxydiphenylene)diquinoline]
4. Poly[2,2'-(p,p'-oxydiphenylene)-6,6'-oxybis(4-phenylquinoline)]
5. Poly[4,6-diphenyl-2,8-(p,p'-oxydiphenylene)-1,9-anthrazoline]
6. Poly[4,9-diphenyl-2,7-(p,p'-oxydiphenylene)-1,6-anthrazoline]

7a. 3,3',4,4'-Tetraaminodiphenyl ether

7b. 3,3'-Diaminobenzidene

8. 4,4'-Oxydibenzil
9. 4,4'-Bis(2-aminobenzoyl)diphenyl ether
10. 4,4'-Bis(2-carboxybenzoyl) diphenyl ether
11. 4-(2-Carboxybenzoyl) diphenyl ether
12. Pseudo-4,4'-Bis(2-carboxybenzoyl)diphenyl ether diacid dichloride
13. 4,4'-Bis(2-carbamylbenzoyl)diphenyl ether
14. 2,3-Diphenylquinoxaline
15. 2,4,6,8-Tetraphenylanthrazoline
16. 2,4,7,9-Tetraphenylisoanthrazoline
17. Triphenylmethyl peroxide
18. Benzoyl peroxide
19. 4,4'-Bis(triphenylmethyl peroxide)
20. 4,4'-Dibenzoyldiphenyl ether
21. 4,4'-Bis(diphenylchloromethyl)diphenyl ether
22. 4,4'-Bis(diphenylmethyl)diphenyl ether

23. Triphenylmethyl hydroperoxide

24. 4,4'-Bis(diphenylhydroxymethyl)diphenyl ether

25. 4,4'-Oxybis(triphenylmethyl hydroperoxide)

26. Poly[4,4'-oxybis(triphenylmethyl peroxide)]

27. 4,4'-Dibenzoyldiphenyl ether dihydrazone

28. 4,4'-Bis(α-diazobenzyl)diphenyl ether

29. Benzophenone hydrazone

30. α-Diazodiphenylmethane

31. 2,2'-(Oxydi-p-phenylene)bis(1,3,4-triphenyldiazocyclopentadiene)

32. 3,3'-(Oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone)

33. 3,3'-(Oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone) tosylhydrazone

34. 3,3'-(Oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone hydrazone

35. 2,2'-(Oxydi-p-phenylene)bis(1,3,4-triphenylcyclopentadiene)

36. Tetraphenylcyclopentadienone tosylhydrazone

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